

Two-dimensional metal-organic frameworks for gas sensing

A thesis submitted for the degree of Doctor of Philosophy



Abigail M. Lister

St. Peter's College

Department of Materials, University of Oxford

Hilary Term 2024

Preface

The research work described in this thesis was carried out by the author, under the supervision of Prof. Martin R. Castell, at the Department of Materials at the University of Oxford, from October 2019 to December 2023. All the work is original and has not been previously submitted for any degree or qualification at this university or any other institute of education. Where the work of other researchers is drawn upon, it has been referenced and acknowledged. Parts of the work described in Chapters 4, 5, 6 and 7 have been presented at international conferences and/or submitted for publication in peer-reviewed journals as follows:

Conferences

Abigail M. Lister, Ben I. Armitage, Yu Wang, Martin R. Castell. ‘New Metal-Organic Framework Synthesis Methods for Optimised Chemiresistive Gas Sensors’, **1st Mediterranean Conference on Porous Materials**, Crete, Greece., 2023. (Oral)

Abigail M. Lister, Ben I. Armitage, Yu Wang, Martin R. Castell. ‘Ultra-sensitive gas sensors made from electrochemically synthesised metal-organic frameworks’, **STEM for Britain 2023 Final**, London, UK., 2023. (Poster). **3rd Place – Engineering category.**

Abigail M. Lister, Ben I. Armitage, Yu Wang, Martin R. Castell. ‘Electrochemical Synthesis of Metal-Organic Frameworks for High Sensitivity Gas Sensing’, **The 5th Annual UK Porous Materials Conference**, Glasgow, UK., 2022. (Oral)

Abigail M. Lister, Ben I. Armitage, Yu Wang, Martin R. Castell. ‘High Sensitivity Gas Sensors Made From Electrochemically Synthesised Metal-Organic Frameworks’, **2022 Innovate UK Materials Research Exchange Conference**, London, UK., 2022. (Poster). **1st Place – Science Technology and Research Quality.**

Abigail M. Lister, Ben I. Armitage, Yu Wang, Martin R. Castell. ‘In-situ Electrochemical Synthesis of Copper Hexahydroxytriphenylene MOF for Chemiresistive Gas Sensing’, **8th International Conference on Metal-Organic Frameworks and Open Framework Compounds**, Dresden, Germany., 2022. (Poster).

Abigail M. Lister, Ben I. Armitage, Yu Wang, Merel J. Lefferts, Weishuo Li, Martin R. Castell. ‘Metal-Organic Framework and Silver Nanowire Composites as Chemiresistive Gas Sensors Operating at the Percolation Threshold’, **18th International Meeting on Chemical Sensors**, Chicago, USA – Virtual., 2021. (Poster).

Abigail M. Lister, Ben I. Armitage, Yu Wang, Martin R. Castell. ‘Chemiresistive Gas Sensors Fabricated from Percolation Networks of Conductive Triphenylene-based Metal-Organic Frameworks and Silver Nanowires’, **RSC Faraday Discussion: MOFs for Energy and the Environment**, UK – Virtual., 2021. (Poster).

Journal Papers

Abigail M. Lister, Ben I. Armitage, Yu Wang, Runze Chen, Weishuo Li and Martin R. Castell. ‘Electrochemically grown $\text{Cu}_3(\text{HHTP})_2$ metal-organic framework from copper nanoclusters for chemiresistive gas sensing’. Submitted for review by **ACS Applied Nanomaterials**.

Abigail M. Lister, Yu Wang, Ben I. Armitage and Martin R. Castell. ‘Conductive metal-organic framework synthesis from metal nanoparticle precursors’. Submitted for review by **IOP Journal of Physics: Materials**.

Thesis word count: 39,000 words

Abstract

Metal-organic frameworks (MOFs) are attractive materials for use in gas sensing applications because of their porosity and high adsorptive site to mass ratios. Through synthesis of conductive MOFs, sensors that respond to analyte gases through a change in electrical resistance can be fabricated. However, the wide-scale use of MOFs as the functional element in electronic devices such as chemiresistors is limited by the absence of methods to reliably synthesise conductive MOFs uniformly and in situ on the desired substrates. In this thesis, methods of synthesising conductive MOFs to overcome these limitations are reported.

Four different conductive MOFs were first synthesised using traditional solution synthesis, $\text{Cu}_3(\text{HHTP})_2$, $\text{Ni}_3(\text{HHTP})_2$, $\text{Cu}_3(\text{HITP})_2$ and $\text{Ni}_3(\text{HITP})_2$. From the resulting powdered MOF samples, chemiresistive sensing devices were fabricated. By analysing the sensing responses to NH_3 and NO_2 analyte gases, it was concluded that the NO_2 interacted permanently with the HHTP-based frameworks via chemical reactions with the lone pairs on the oxygen atoms in the ligand, whilst the NH_3 analyte interacted with the metal centres either directly with the metal, or indirectly via coordinated H_2O . Experiments comparing sensors of the same $\text{Cu}_3(\text{HHTP})_2$ MOF with different particle morphologies showed that flatter flake-like MOF crystals gave a superior limit of detection than sensors of the same MOF composed of hexagonal crystals. This work provides sensing performance benchmarks to which sensors made from subsequent methods can be accurately compared. It also reveals the significant morphological dependence of the sensing performance of these MOF systems.

The same four MOFs were subsequently synthesised in an inverse opal structure using polystyrene nanosphere templates to probe the effect of this morphology on the sensing performance. The resulting hierarchically porous $\text{Ni}_3(\text{HHTP})_2$ MOF structure was found to

respond with a reversible increase in resistance when exposed to NH_3 , whilst the same MOF synthesised via traditional solution synthesis showed no response. Contrastingly, the hierarchically porous $\text{Cu}_3(\text{HITP})_2$ MOF responded to NH_3 with a multicomponent response comprised of a reversible resistance increase and irreversible resistance decrease, when only a reversible resistance increase was observed for a sensor made from the same MOF synthesised with traditional methods. These differences are rationalised in terms of morphology, reaction mixture alkalinity, and inclusion of Cl from the reaction solution. This work reveals that the sensing behaviour and reversibility of sensing responses of these MOFs can be changed by changing the synthesis conditions. This is an important insight necessary to inform the design of MOFs for reversible gas sensing or irreversible gas storage.

A new method to synthesise two conductive MOFs in situ on a variety of substrates from metal nanoclusters is also presented. Copper and nickel nanoclusters were deposited onto substrates to act as the metal source for MOF formation when submerged in an alkaline solution of ligand and electrolyte. This method successfully generates uniform distributions of the desired MOFs in situ on glass, gold, paper and cotton substrates, and is therefore anticipated to be a significant finding in the fields of wearable electronics, chemiresistive sensors and capacitor devices.

To reduce the contribution of inter-particle contact resistance to the measured resistance of the MOF sensors, a method to electrochemically synthesise a MOF from metal nanoclusters was then developed. By depositing copper nanoclusters onto inter-digitated electrodes, and performing chronomamperometry in a solution of the ligand, the desired Cu-based MOF was grown in situ on the electrodes required for sensing experiments. The resulting sensors were able to detect NH_3 gas with concentrations in the ppb range. This makes the electrochemically-synthesised MOF sensors competitive with the performance of metal oxide semiconductor sensors in terms of limit of detection. Beyond the processing and uniformity advantages, the

fabricated MOF sensors are also able to operate at room temperature, whilst metal oxide semiconductor NH_3 sensors typically require operation temperatures of at least 150 °C. The electrochemically-synthesised MOF sensors showed enhanced linearity in response compared to the analogous sensors made from MOF powders, and would therefore make more reliable real-world sensors.

Acknowledgements

I owe a huge amount to my supervisor, Professor Martin Castell, for his support and guidance throughout this project. I have learnt a lot from him during my time in Oxford and for that I am incredibly grateful. I also owe particular thanks to Ben for training and guiding me throughout the start of my DPhil, his input has been crucial to the development of this project and without his initial direction I feel I may have been quite lost! I would also like to thank my colleagues and friends from the Surface Nanoscience group; Merel, Weishuo, Yu, Runze, Sparsh, and Zirui. It has been a pleasure to get to know them and I am very grateful for both their scientific advice and their friendship.

I am very grateful to the EPSRC for providing me with a DTP award to fund this work, without which I would have not have been able to start this project. I would also like to thank the members of the David Cockayne Centre for Electron Microscopy (DCCEM), Jennifer Holter, Phani Karamched, Neil Young and Ian Griffiths for training me on the use of their SEM machines, and for their assistance with TEM imaging. I also wish to thank the Oxford Materials Characterisation Service, particularly Wai Man for assistance with XPS, as well as Colin Johnston and Philip Holdway. I am also very grateful for the assistance from Srinivasa Rao Saranu from Nikalyte Ltd, without whom the nanocluster deposition with the NL50 system would not have been possible.

I am beyond grateful for my loving family; my parents, sister and grandparents. Their support has been instrumental in getting me to a place where I can undertake this DPhil. I am also very thankful for the friends both new and old who I have enjoyed times with throughout the last four years. I would like to thank my wonderful housemates Sorch, Jodie and Megan, as well as Izzy, Hannah, Alice and the rest of the Newnham gang for both supporting and inspiring me throughout my time in Oxford. To my longest standing school friends Zoe, Rachel and

Jess, I am so grateful for the fun we have had during what could otherwise have been a very stressful time. I must finally acknowledge the adventures that I have had with members of the Oxford University Yacht Club, it has been a joy to learn from, compete alongside, and most importantly laugh with all of you.

Contents

Preface	2
Abstract	4
Acknowledgements.....	7
Contents.....	9
1. Introduction.....	13
2. Literature Review.....	18
2.1 Metal-Organic Frameworks.....	18
2.1.1 Uses of MOFs.....	27
2.2 MOF gas sensors.....	30
2.2.1 Optical MOF sensors.....	31
2.2.2 Mechanical MOF sensors.....	34
2.2.3 Electronic MOF sensors.....	36
2.3 Electronically conductive MOFs.....	39
2.3.1 Through-bond charge transport.....	42
2.3.2 Extended conjugation	43
2.3.3 Through-space charge transport.....	44
2.3.4 Redox hopping.....	45
2.3.5 Guest-promoted charge transport.....	46
2.4 Hexa-substituted triphenylene MOFs.....	48
2.4.1 Structure and conductivity.....	48
2.4.2 Synthesis methods and device integration	55
2.4.3 Chemiresistive sensing of HXTP MOFs.....	60
2.5 Sensing mechanisms	63
2.6 Conclusion.....	66
3. Experimental techniques.....	68
3.1 Sensor fabrication.....	68
3.1.1 Solution synthesis of conductive MOFs.....	68
3.1.2 Interdigitated electrodes and drop casting	71

3.1.3 Metal nanocluster deposition.....	72
3.1.4 Chronoamperometry.....	76
3.1.5 Cyclic voltammetry.....	77
3.2 Characterisation techniques.....	78
3.2.1 Electron microscopy.....	79
3.2.2 Powder X-ray diffraction.....	80
3.2.3 Transmission electron microscopy	81
3.2.4 Raman spectroscopy	82
3.2.5 X-ray photoelectron spectroscopy	83
3.3 Sensing techniques.....	84
3.3.1 Sensing chamber set-up.....	84
3.3.2 Sensor performance assessment	87
4. Synthesis and sensing performance of solution-synthesised MOFs	89
4.1 Context	89
4.2 HHTP MOFs.....	90
4.2.1 Synthesis.....	91
4.2.2 Characterisation	91
4.2.3 Sensing response of HHTP MOFs to NH ₃	96
4.2.4 Sensing response of HHTP MOFs to NO ₂	99
4.3 HITP MOFs.....	102
4.3.1 HITP MOF synthesis.....	102
4.3.2 HITP MOF characterisation.....	102
4.3.3 Sensing response of HITP MOFs to NH ₃	105
4.3.4 Sensing response of HITP MOFs to NO ₂	107
4.4 Sensing mechanism	109
4.5 Conclusion	114
5. Synthesis of conductive metal-organic frameworks via metal nanocluster submersion	
5.1 Context	115
5.2 Materials and methods	117
5.3 Method development	118
5.4 MOF growth	122

5.5 Substrate investigations	129
5.6 Characterisation	131
5.6.1 X-ray photoelectron spectroscopy	132
5.6.2 Powder X-ray diffraction	136
5.6.3 Transmission electron microscopy	137
5.7 Conclusion	138
6. Electrochemical growth of $\text{Cu}_3(\text{HHTP})_2$ from copper nanoclusters for chemiresistive gas sensing.....	140
6.1 Context	141
6.2 Methodology	142
6.2.1 Method in theory	142
6.2.2 Experimental protocol	144
6.3 MOF growth	145
6.4 Characterisation	148
6.4.1 Powder X-ray diffraction	148
6.4.2 X-ray photoelectron spectroscopy	150
6.4.3 Raman spectroscopy	152
6.4.4 Cyclic voltammetry	154
6.5 Sensing behaviour	156
6.6 Conclusion	160
7. Templated synthesis of conductive MOFs for hierarchically porous sensors	162
7.1 Context	162
7.2 Materials and methods	164
7.3 Characterisation	166
7.3.1 Scanning electron microscopy	166
7.3.2 Energy dispersive X-ray analysis	171
7.3.3 X-ray photoelectron spectroscopy	173
7.4 Sensing responses	179
7.4.1 Sensing behaviour of $\text{Cu}_3(\text{HHTP})_2$	179
7.4.2 Sensing behaviour of $\text{Cu}_3(\text{HITP})_2$	184
7.4.3 Sensing behaviour of $\text{Ni}_3(\text{HHTP})_2$	186

7.4.4 Sensing behaviour of $\text{Ni}_3(\text{HITP})_2$	189
7.5 Conclusion	189
8. Summary and future outlook	192
8.1 Scientific progress.....	192
8.2 Implications of research	195
8.3 Broader outlook	197
8.4 Future work.....	198
References	201

Chapter 1

Introduction

The demand for effective gas sensors has grown with society's increasing awareness of the threats that invisible and odourless gases can pose. Research in the field of gas sensors has undergone considerable growth in recent years. As of 2022, the global gas sensor market was valued at 1.5 billion USD and is predicted to continue to rise in value over the next decade.¹

Many of us are already exposed to gas sensors on a daily basis in the form of smoke alarms and carbon monoxide detectors, but as technology and medical research develop, they are likely to play an increasingly visible role in our lives. A variety of gas sensing systems are available to purchase online from companies such as Bertin or Omnia Instruments. These ordinarily utilise spectroscopic detection techniques such as infrared spectroscopy, mass spectrometry or ion-mobility spectrometry, wherein equipment records variations in a continuous variable across a spectrum and identifies substances by comparing them to database records. Such spectroscopic identification methods are accurate but typically require an additional pre-concentration step² and are generally bulky, costly, and unsuitable for high sensitivity continuous remote monitoring of environments.³ Alternative sensing systems in which changes in a sensor's electrical, mechanical or optical properties are measured in real-time during exposure to an analyte present promising alternatives to spectroscopic detection systems.

Sensors that respond to changes in resistance on analyte adsorption, chemiresistive sensors, are widely used sensing media in commercially-available devices. Chemiresistive sensors using metal oxide sensing media can be purchased, but are disadvantaged by the high

operating temperatures that they require (typically around 300 °C).⁴ As such, alternative chemiresistive sensing systems have been investigated, with conducting polymers attracting particular attention, but hurdles have been presented in the form of poor humidity tolerance and limited lifespans.⁵

Porous frameworks made up of metal nodes and organic linkers, Metal-Organic Frameworks, MOFs, are attractive materials for use in gas sensing devices. Renowned for their high internal surface areas and tuneable chemical functionalities, MOFs have generated significant interest as potential materials for gas sensing directly from the atmosphere.⁶ Some conductive MOFs are able to trap gaseous analytes in their pores resulting in a measurable change in conductivity, enabling them to act as chemiresistive sensors. Conductive MOFs are typically synthesised as microcrystalline powders which are then drop-cast onto the desired substrates. This often results in inhomogeneous MOF distributions, high inter-particle contact resistances and poor substrate adhesion. To aid in their integration into electronic devices such as chemiresistive sensors, there is therefore a need for synthesis methods that can reliably generate uniform distributions of the MOFs in situ on the desired substrates. The work in this thesis aims to address these needs by developing new methods of synthesising conductive MOFs, with the view to accelerating progress towards the use of conductive MOFs in real-world devices.

The thesis begins with a literature review on the topic of MOFs. This starts with a broad description of the principles of MOF design and a survey of some of the common uses of MOFs. The particular appeal of MOFs for use in gas sensing applications is highlighted and the ways in which they have been incorporated into optical, mechanical and electronic gas sensors is explored. The mechanisms that can lead to conductivity in MOFs are then described, before a description of the structure and conductivity of the specific class of MOFs focused

on in this thesis. Reported synthesis methods of these conductive MOFs are summarised preceding a description of their previous use in chemiresistive sensing devices. The chapter concludes with a summary of the potential sensing mechanisms that could be responsible for their chemiresistive responses.

Chapter 3 gives an introduction to the experimental methods used in carrying out the work described. This includes the protocols used for the solution synthesis of conductive MOFs, complete with the chemicals and suppliers. The inter-digitated electrodes used are then described. This is followed by information about the magnetron sputtering source used to deposit metal nanoclusters on various substrates. The chronoamperometry technique performed to electrochemically synthesise MOFs from the metal nanoparticles is then explained. Sample characterisation is vital to the work in this thesis to confirm that the new synthesis methods developed have successfully made the desired MOFs. A description of the working principles and experimental conditions used in cyclic voltammetry, powder X-ray diffraction, transmission electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy and scanning electron microscopy are given. Finally, the set-up of the sensing experiments is described, and the methods of extracting figures of merit, such as sensitivity and limit of detection, from the sensing data are explained.

Chapter 4 is the first experimental chapter and describes the solution synthesis of 4 conductive MOFs. Their morphologies are compared with SEM and their sensing responses to NH_3 and NO_2 analyte gases are analysed. By comparing the responses of the four MOFs it is concluded that interactions with NO_2 likely occur via chemical reactions with lone pairs of ligand oxygen atoms. Analysis of the chemiresistive responses of the same sensors to NH_3 allowed us to confirm that these interactions likely occur directly with the metal centre, or indirectly by interacting with a coordinated H_2O molecule.

Chapter 5 focuses on the development of a method to synthesise two conductive MOFs in situ on glass, gold, cotton and paper substrates. A room temperature magnetron sputtering source is used to deposit metal nanoclusters onto the substrates. These nanoclusters then function as the metal source for conductive MOF formation. Time-point SEM and optical images are analysed to give an insight into the progress of MOF growth. The MOFs are characterised with XPS, PXRD and TEM. The method was successful in generating MOF on all of the substrates used, and it is anticipated to work on any substrate that will fit inside the nanocluster deposition chamber. The versatility of substrates that the method works on, combined with the mild synthesis conditions, is anticipated to make this method useful for direct growth of conductive MOFs on fragile electronic components.

Chapter 6 again involves the use of a magnetron sputtering source to deposit metal nanoclusters to be used in MOF synthesis. This time they are deposited onto inter-digitated electrodes which are then used to grow a Cu-based MOF via an electrochemical method. The MOF is characterised with SEM, PXRD, XPS and Raman spectroscopy. The electrochemically synthesised MOF was found to detect NH_3 with a limit of detection of 0.158 ± 0.006 ppm, a value lower than the majority of metal oxide-based NH_3 sensors.⁷ In addition to the superior limit of detection, the electrochemically-synthesised sensor achieves this value at room temperature, whilst metal oxide sensors often require heating to a constant temperature between 200 and 400 °C.⁸

Chapter 7 is the final experimental chapter and describes the templated synthesis of all 4 MOFs discussed in the previous chapters around polystyrene nanospheres. After the MOFs have been produced, the nanospheres are dissolved to leave inverse opal MOF structures. The performances of the resulting MOFs as NH_3 and NO_2 sensors are then assessed. The $\text{Cu}_3(\text{HITP})_2$ MOF sensor made with this method was found to give a response with irreversible

and reversible components, whilst the solution synthesised MOF showed only reversible behaviour. In addition, it was found that the $\text{Ni}_3(\text{HHTP})_2$ MOF synthesised with this method responded to NH_3 with reversible resistance increases whilst the same MOF synthesised via solution synthesis showed no response. This is of significance as to our knowledge, chemiresistive responses to NH_3 by this MOF have not been observed before. This finding suggests that changing the synthesis conditions and/or particle morphology can promote sensing responses, something that is expected to have implications in the future of MOF sensor design.

In chapter 8 the results of the work described in this thesis are summarised and their implications are discussed. The work described presents significant steps forward in enabling MOFs to be integrated into electronic devices, with potential uses in wearable toxic gas sensors and exhaled breath devices for medical applications. The MOF synthesis methods described in chapters 5, 6 and 7 provide significant advantages over the solution-synthesised MOF benchmarks provided in chapter 4. These advantages are highlighted in chapter 8 and where appropriate, the sensors fabricated in this thesis are compared to other chemiresistive sensing materials such as metal oxide semiconductors.

Chapter 2

Literature Review

The aim of this DPhil is to develop effective metal-organic framework gas sensors, and new metal-organic framework synthesis methods to improve their applicability in electronic devices. In this chapter, the relevant prior art is discussed. It starts with a discussion of traditional 3D MOFs and their reasons for use in gas sensing. In section 2.3, conductivity in MOFs is introduced, alongside different synthetic routes for producing 2D conductive MOFs. Previous reports of such conductive 2D MOFs in chemiresistive gas sensing is then covered, whilst in section 2.5, studies to uncover the sensing mechanisms taking place for the MOFs focused on in this thesis are described.

2.1 Metal-organic frameworks

The term ‘metal-organic framework’ was first used by Yaghi et al. in 1995 to describe the extended framework structure formed when copper nitrate hydrate and 4,4’-bipyridine were reacted under hydrothermal conditions.⁹ The term, frequently abbreviated to ‘MOF’, describes the structure formed when organic ligands link metal-containing groups called secondary building units, SBUs, to create permanently porous frameworks.¹⁰ The organic and metal-containing moieties are joined by chemical bonds to produce reticular frameworks. MOFs with different ligands or metal SBUs that have the same underlying framework net are described as isorecticular.¹¹ The formation of MOFs from their constituent building blocks can be represented in its simplest level with a diagram such as that in Figure 2.1, reproduced from the 2021 publication by Singh. et al.¹²

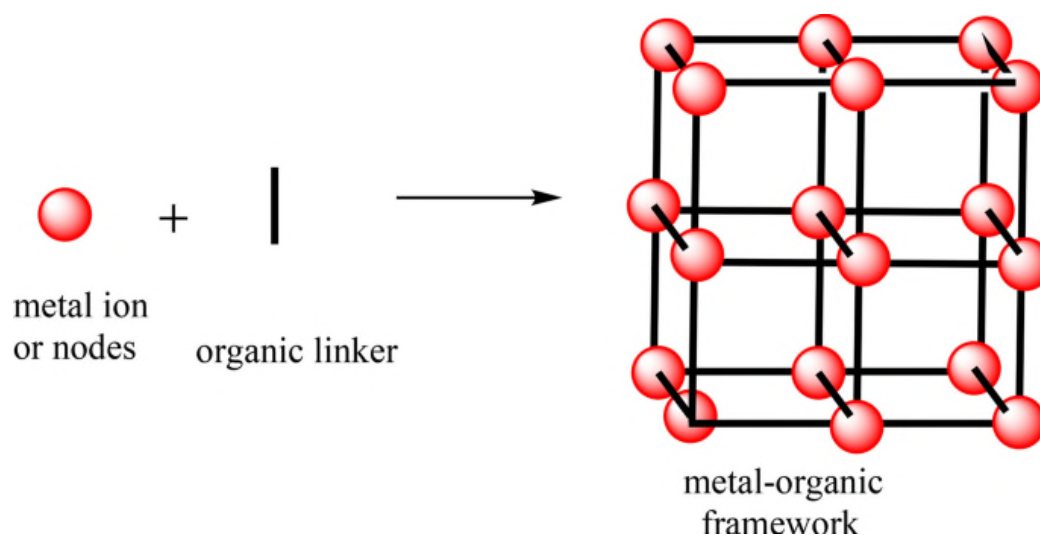


Figure 2.1: Schematic illustration of the formation of a 3D MOF from its constituent metal nodes and organic linkers. 3D MOF structures can form from solutions of their components via self-assembly. Reproduced from reference 12.

By changing the ligand and/or metal SBU, different MOFs can be obtained. As of 2020, over 100,000 different MOF structures had been reported.¹³ MOFs have been synthesised using a huge variety of organic linkers as the ligands, many of which use oxygen, nitrogen and sulphur atoms as part of the groups responsible for binding to the metal. Examples of such ligands can be seen in Figure 2.2. Typically, ligands used in MOF synthesis involve functional groups that can be deprotonated in solution to facilitate bonding to a positively charged metal ion in more than one place on the ligand. In addition, they are often based on planar structures such as benzene, as this rigidity in structure lends itself to the formation of ordered networks.

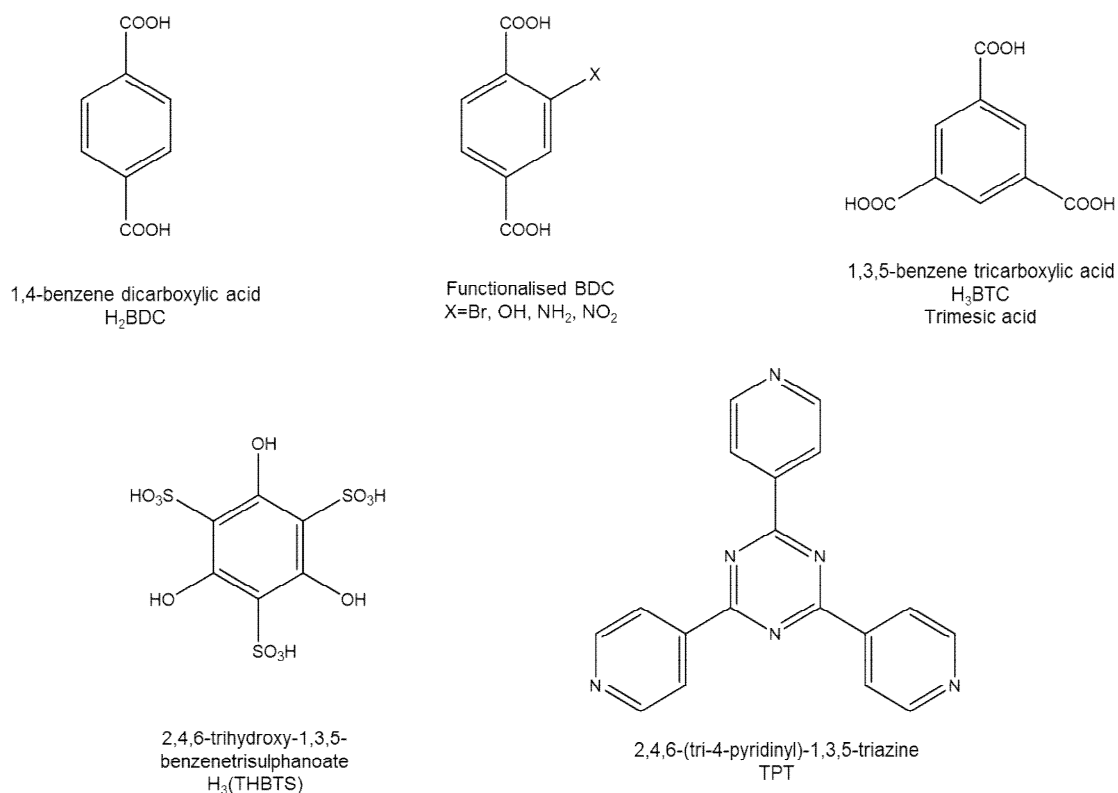


Figure 2.2: The structures of 5 organic precursors known to form linkers in metal-organic frameworks. All pictured molecules must undergo some deprotonation in order to be incorporated into the MOF, apart from TPT (bottom right) which can act as a linker in its pictured form.

The BDC ligand at the top left of Figure 2.2 will be deprotonated at both of the carboxylic acid groups enabling it to bridge two different metal SBUs to form 3D MOFs such as $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC})_6$, commonly referred to as UiO-66.¹⁴ Subsequent research has found that MOFs with the same framework structure can be synthesised from BDC ligands with additional functionalities on the benzene in position X, as depicted at the top of Figure 2.2. Br, NH₂ and NO₂ groups have all been successfully added without altering the two-coordinate nature of the ligand.¹⁵ The result of this is that additional functional groups not involved in framework bonding are introduced into the structure, as depicted in Figure 2.3.¹⁵ This has enhanced the potential applications of MOFs in the UiO-66 family. UiO-66-NH₂ for example, was found to more effectively adsorb cationic dyes from aqueous solution than its' UiO-66 counterpart.¹⁶

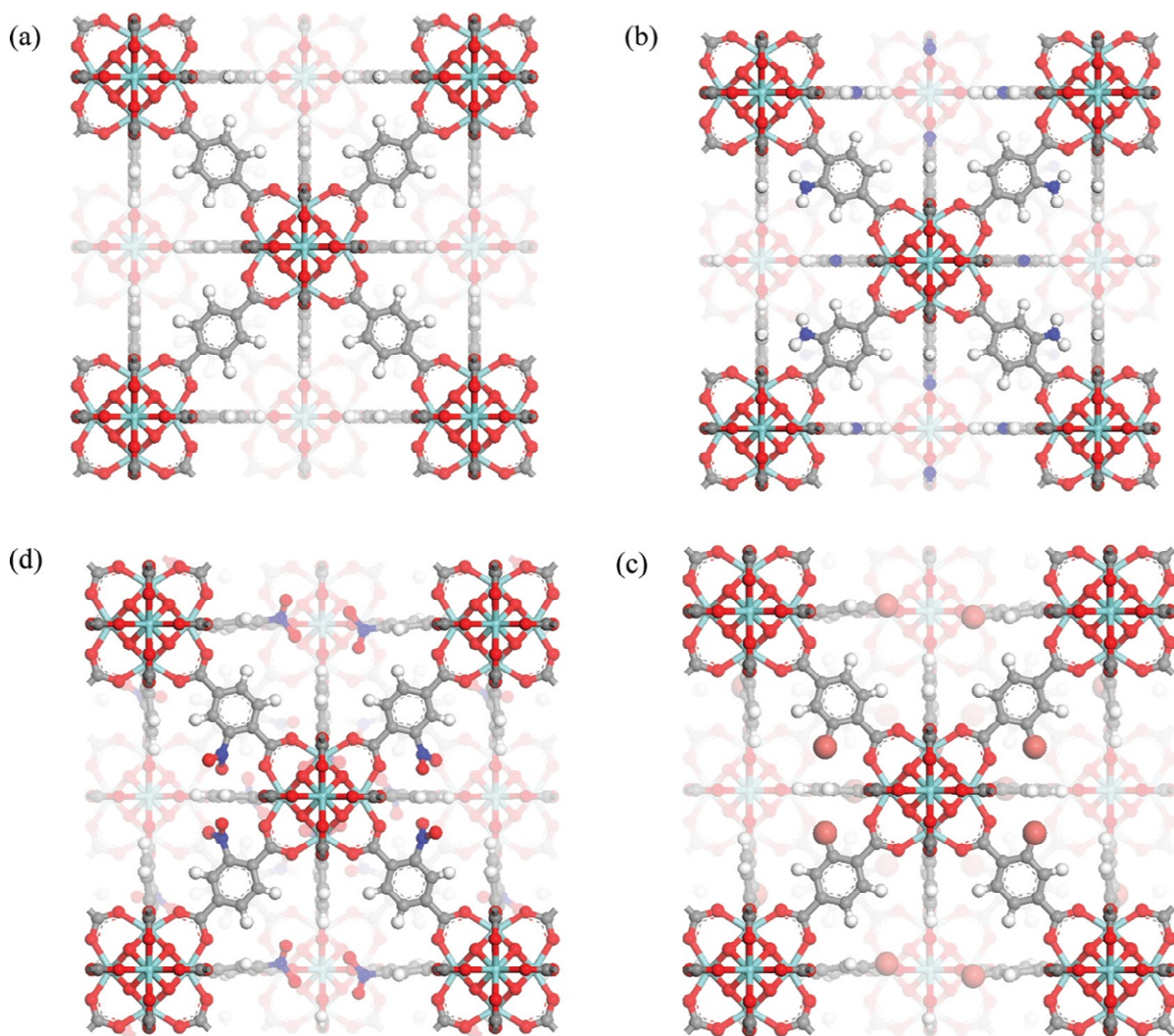


Figure 2.3: Structures of the UiO-66 family of MOFs comprised of $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters linked by benzenedicarboxylate linkers with different functionalities. **Key:** C (grey), H (white), O (red), Zr (cyan), N (purple), Br (large orange). **(a)** UiO-66 MOF containing 1,4-benzene-dicarboxylate linkers. **(b)** UiO-66- NH_2 containing 2-amino-1,4-benzene-dicarboxylate linkers. **(c)** UiO-66- NO_2 containing 2-nitro-1,4-benzene-dicarboxylate linkers. **(d)** UiO-66-Br containing 2-bromo-1,4-benzene-dicarboxylate linkers. The MOFs depicted in (b), (c) and (d) contain ligand functional groups that are not involved in MOF formation and are therefore available to interact with guest molecules. Reproduced from reference 15.

The H₃BTC and TPT organic precursors depicted in Figure 2.2 can both facilitate bonding to 3 different metal SBUs to form MOFs. The MOF synthesised from BTC³⁻ and Cu₂(CO₂)₄ paddle wheel units has been widely studied since its first reported synthesis.¹⁷ More recently, researchers have fabricated mixed metal MOFs with the same ligand, whereby some of the Cu²⁺ ions in the original Cu-BDC MOF, Figure 2.4, were substituted for Ni²⁺, Zn²⁺, Co²⁺ or Fe²⁺ ions via post-synthetic ion exchange.¹⁸ The resulting M-Cu-BDC MOFs were found to have H₂ adsorption capacity approximately 60 % higher than that of the original Cu-BDC MOF.¹⁸

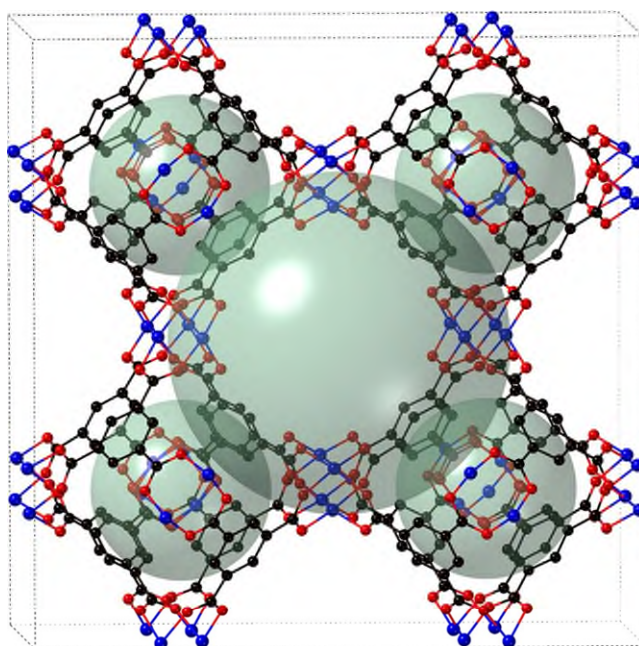


Figure 2.4: The structure of a Cu-BTC MOF, also referred to as HKUST-1, as viewed down the z-axis. **Key:** C (black), O (red), Cu (blue). The green spheres represent porous cavities in the MOF. Post-synthetic ion exchange enables some of the Cu centres (blue) to be replaced with Zn, Ni or Co centres. This results in higher H₂ storage capacities. Reproduced from reference 18.

The THBTS ligand depicted in Figure 2.2 forms a 3D MOF on reaction with sodium bicarbonate.¹⁹ Each ligand molecule bonds to three different Na⁺ ions. The Na⁺ ions are described to be 8-coordinate, forming 6 bonds to sulphonate oxygen atoms, and two to hydroxyl oxygens. The resulting MOF is comprised of hexagonal sheets that are cross-linked

to Na^+ in the third dimension to form a structure with 1D pore channels, Figure 2.5.¹⁹ Shimizu et al. found that introducing triazole molecules into the pores enhanced the proton conducting ability of the MOF.¹⁹ The ability of some MOFs to facilitate proton conduction by inclusion of particular guests or through the MOF itself, is of interest to those looking to fabricate solid state proton conductors for the fuel cell industry. As such, a significant amount of work has been performed in this field, with a number of review articles recently published.^{20,21,22,23}

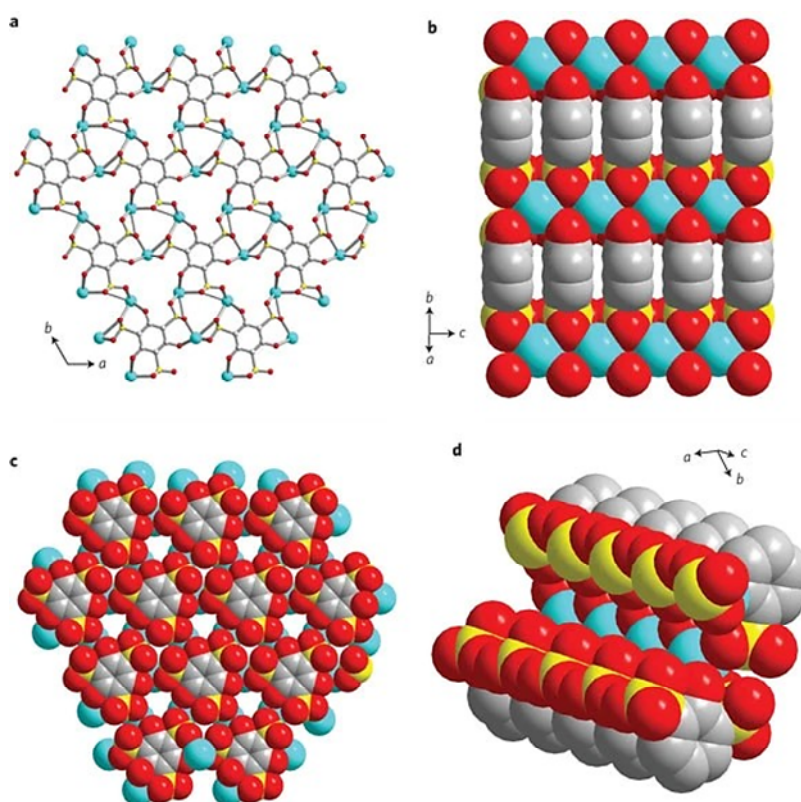


Figure 2.5: Structure of the β -PCMOF2 produced from reaction of sodium bicarbonate with 2,3,6-trihydroxy-1,3,5-benzenetrisulphanate reported by Shimizu et al. **Key:** C (grey), O (red), S (yellow), Na (cyan). **(a)** Ball and stick representation of a single layer of β -PCMOF2. **(b)** Space-filling diagram viewed perpendicular to the pores. **(c)** Space-filling diagram viewed down the pore axis. **(d)** Space-filling diagram of a single pore cross-section, showing how sulphonate groups line the pores. The MOF conducts protons in its depicted form, but loading it with 1H-1,2,4-triazole molecules was found to enhance the proton conducting ability. Reproduced from reference 19.

Changing the functionality or length of the linker is key in determining the geometry of the pores in the final MOF, with longer linkers typically resulting in larger pores.¹⁰ MOFs can be

labelled as micro-, meso- or macro- porous depending on the diameters of their pores. Typically, microporous MOFs have pore diameters less than 2 nm, mesoporous MOFs have pore diameters between 2 and 50 nm, and macroporous MOFs have pore diameters greater than 50 nm.²⁴ By keeping the linker functionality the same but by adding phenyl groups to lengthen it, it can be possible to synthesise isorecticular MOFs with different pore diameters.²⁴ This approach was pioneered by Yaghi et al. in 2002 when they synthesised MOFs made from octahedral Zn-O-C clusters and carboxylate functionalised linkers of different lengths to form isorecticular MOFs with pore diameters between 3.8 and 28.8 Å.²⁵ The MOFs with the largest and smallest diameters made in these experiments are depicted in Figure 2.6.²⁵ By comparing the crystal structures of the two MOFs depicted in Figure 2.6, we can see that on changing the linker from 1,4-benzenedicarboxylate to p-terphenyl-4,4''-dicarboxylate, the cubic MOF structure is retained but the pore diameter and volume is increased. Similar experiments have since been performed for numerous other MOF systems.^{26,27,28}

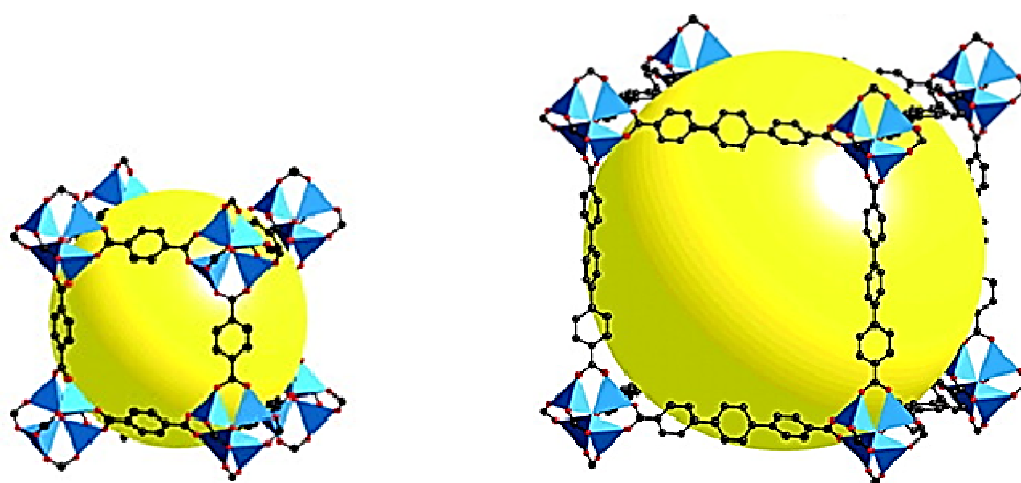


Figure 2.6: *Left* - Representation of the crystal structure of IRMOF-1 made from Zn-O-C clusters and 1,4-benzenedicarboxylate linkers. *Right* – Representation of the crystal structure of IRMOF-16 made from the same Zn-O-C clusters and longer p-terphenyl-4,4''-dicarboxylate linkers. **Key:** Zn (blue polyhedra), O (red), C (black). The yellow spheres are reflective of the pore volume. Increasing linker length results in larger pore volumes. Figure is not to scale and is a modified section of Fig. 1 from reference 25.

MOFs with larger pores are often desired because they can offer more gas storage volume and more active sites per unit mass. However, increasing the pore diameter via ligand extension

comes with a risk of producing less stable frameworks, an effect that is more common for frameworks involving relatively soft Lewis acid metals such as Cu^{2+} and Zn^{2+} .²⁹ It is not uncommon for MOFs with larger pore dimensions to only be stable when loaded with particular guests, and thus be susceptible to collapse when the guests are removed.²⁸ There is also a greater risk of forming interpenetrating MOF structures as the linker is extended. Such structures involve the interlocking of two or more different lattices within one MOF crystal,³⁰ as represented schematically in Figure 2.7.³⁰ This is typically an undesired phenomenon, as the formation of interpenetrated lattices reduces the size of the accessible pore aperture,²⁸ although for some applications interpenetrating structures offer advantages.^{31,32} Strategies explored to reduce the likelihood of forming interpenetrating structures and increase the stability of MOFs with larger pore diameters include adding bulky substituents to the ligand backbone,³³ controlling the reaction temperature and concentration,³⁴ and introducing solvents or counter-ions to act as temporary space-filling templates.^{32,35}

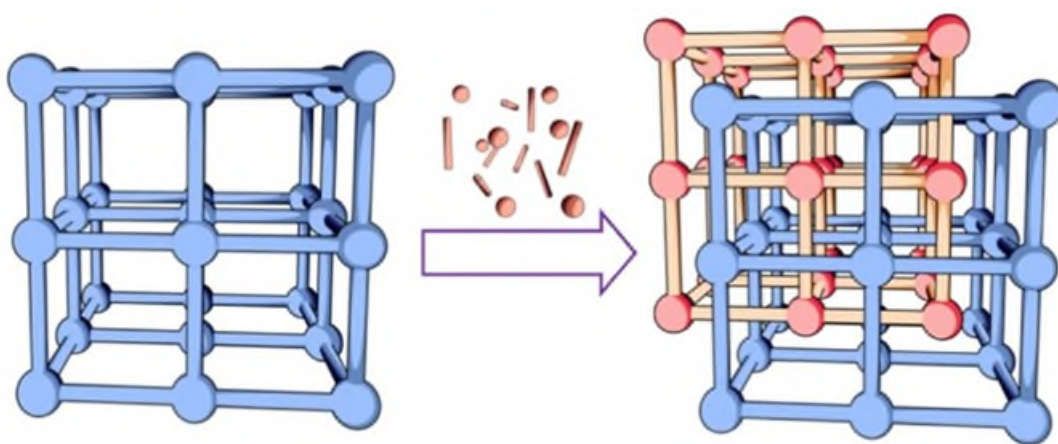


Figure 2.7: Schematic to illustrate how on addition of further MOF reactants, an additional MOF lattice (red) can form interlocked with the original MOF lattice (blue). The red and blue lattices are not chemically bonded to each other. This is more common when longer ligands are used. Reproduced from reference 30.

There are a wide range of metal-containing units that can function as nodes in MOFs, including single metal ions, metal carboxylate groups and metal-nitrogen groups.³⁶ For example, single metal ions such as Cu^{2+} , Co^{2+} , Ni^{2+} and Fe^{2+} can be reacted with triphenylene-

based MOFs to form 2D hexagonal MOF sheets that can stack to form 3D structures.³⁷ Similarly, single Eu^{3+} ions from $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ salt are reported to form a 3D MOF when reacted with oxalic acid ligands in the presence of a dimethyl ammonium template.³⁸ Metal carboxylate clusters are also common SBUs for MOF formation. Paddlewheel metal clusters with the general formula $\text{M}_2(\text{COO})_4$ appear often in MOF structures.³⁶ For example, the square $\text{Cu}_2(\text{COO})_4$ group forms the well-studied 3D HKUST-1 MOF when reacted with benzene-1,3,5-tricarboxylate linkers, Figure 2.4.¹⁸ In the starting salt, each Cu in the paddle wheel unit is present in a square pyramidal geometry where it is bonded to four carboxylate oxygen atoms, and one coordinating water molecule. On formation of MOFs such as MOF-11, synthesised from Cu paddle wheels and 1,3,5,7 – adamantane tetracarboxylate ligands, the coordinated water is removed leaving open metal sites, which is significant for applications such as catalysis and gas absorption.³⁹ Other common carboxylate SBUs include octahedron-shaped $\text{Zn}_4\text{O}(\text{COO})_6$ ⁴⁰ and $\text{Fe}_3\text{O}(\text{COO})_6$ trigonal prisms.⁴¹ Schematic representations of example metal carboxylate SBUs are depicted in Figure 2.8.³⁶ Instead of metal carboxylate clusters, clusters of metal ions and coordinated nitrogen-containing compounds can be used as SBUs. Neutral compounds based on pyridine or anionic nitrogen containing species such as triazole can be used to form these units.^{36,42}

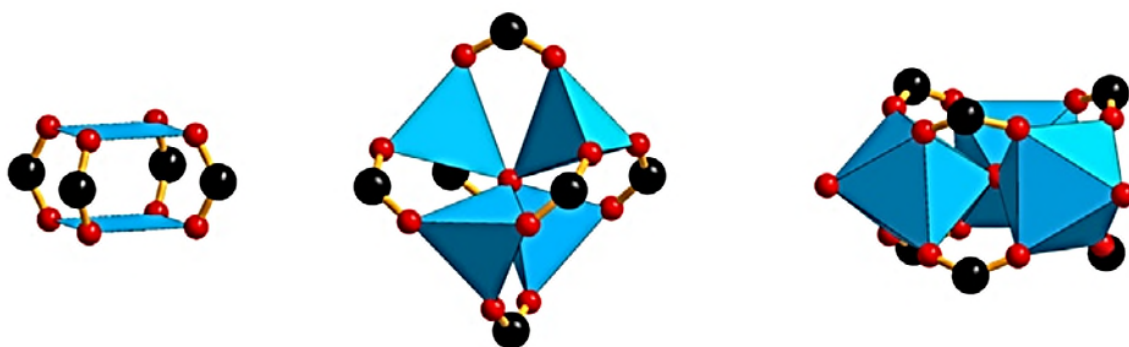


Figure 2.8: Schematic representation of common metal-carboxylate SBUs present in MOFs. **Left** – 4-coordinate $\text{M}_2(\text{COO})_4$ paddlewheel. **Centre** – 6-coordinate $\text{M}_4\text{O}(\text{COO})_6$. **Right** – 6-coordinate $\text{M}_3\text{O}(\text{COO})_6$. **Key:** Metal (blue polyhedra), O (red), C (black). The rest of the linker molecule extends from each black carbon atom to continue the framework. Figure is a reproduced subsection of Figure 2.2 from reference 36.

There are now reported syntheses of MOFs based on a large number of metals across different blocks of the periodic table. These include lanthanides like Nd and Pr,⁴³ group 1 metals like Na and Li,⁴⁴ alkaline earth metals such as Sr and Ba,⁴⁵ p-block metals such as Al⁴⁶ and In,⁴⁷ and a number of the transition metals. This large choice in metal ions, metal cluster types, ligand functionalities and ligand lengths, means that MOFs lend themselves to systematic design for particular applications. MOFs have therefore been investigated as the active material across a wide variety of applications, some of which will be highlighted in the following section.

2.1.1 Uses of MOFs

The structural and chemical versatility of MOFs have meant that they have been explored for a number of different applications. Most of the investigated uses of MOFs can be grouped into the categories of gas storage and capture, water purification, drug delivery, catalysis or energy materials.

MOFs have attracted attention as potential materials for storage of fuel gases such as CH₄ and H₂, in order to store larger masses of gas at higher temperatures or lower pressures than in traditional gas cylinders.^{48,49,50,51} Similarly, MOFs have been investigated for use in removing and storing CO₂ gas from the atmosphere⁵² and for capture of toxic gases such as SO₂, H₂S and NO_x.⁵³ A team lead by Omar Farha in the United States now develop MOF/fibre composites in collaboration with the military to produce clothing and masks that can both capture and deactivate chemical threats, such as nerve agents, in the air.⁵⁴

Water-stable MOFs have been investigated for use in water purification technologies, both as filtration membranes to capture and remove chemicals from water as it passes through, and as simple chemical or physical adsorbents.⁵⁵ Substances such as dyes,¹⁶ heavy metal ions,⁵⁶

antibiotics⁵⁷ and radionuclides⁵⁸ have all been removed from water using MOFs. In addition to water purification, MOFs have also been utilised for water harvesting.^{59,60} Of particular note is the device fabricated by Yaghi et al. that is able to harvest atmospheric water in low-humidity environments like deserts. The device uses a MOF based on Al centres linked by pyrazine-2,3-dicarboxylate ligands, MOF-303, to capture water from the air without the need for energy input other than natural sunlight. An average of 114 g of H₂O per kg of MOF per day was harvested when the device was tested in Death Valley, California in August 2022.⁶¹

MOFs have also been investigated for use in biomedical applications, with a particular focus on drug delivery systems. MOFs have been found to encase antibiotics,⁶² neurotransmitters⁶³ and larger biological molecules such as nucleic acids and proteins.⁶⁴ The drug or biological molecules can be incorporated into the MOF pores at the synthesis stage, with the MOF self-assembling around the drug, or allowed to diffuse into the MOF pores from solution after MOF synthesis. Release of the drug can be triggered by MOF decomposition caused by changes in pH, exposure to UV light or the presence of biological compounds such as ATP.⁶⁴ Whilst many successful laboratory experiments have been performed in this area, there are no reported uses of MOFs in clinical trials.

The high internal surface areas and consequent high densities of active sites have made MOFs attractive candidates for catalysis.⁶⁵ MOFs have been reported to catalyse a wide variety of reactions including CO₂ reduction,⁶⁶ H₂ production,⁶⁷ polymerisation⁶⁸ and alcohol oxidation.⁶⁹ Recent advances in this field include fabricating multifunctional MOF catalysts through adding functional groups to the ligands in the MOF, allowing the MOF to act as a catalyst for different stages of tandem reactions.⁷⁰ Not all MOFs are able to act as catalysts, but many have been used to immobilise catalytic species or encapsulate species such as catalytic nanoparticles.⁷¹ This prevents unfavourable agglomeration of the nanoparticles, whilst the porous nature of the MOF still enables reactants to diffuse to the nanoparticles.⁷²

Diffusion of the reactants can be further enhanced by introducing specific functional groups, such as hydrophobic groups, to the MOF linkers.⁷² The same principles have recently been extended to biological systems. Man et al. report success in encapsulating multiple enzymes in different shells of ZIF-8 MOF. They were able to host incompatible enzymes in the same MOF particle but in different MOF shells by using epitaxial shell-by-shell overgrowth. This allowed incompatible-enzyme cascade reactions to occur within the same MOF particle.⁷³

MOFs have also been used to perform a number of roles within batteries.⁷⁴ They have been employed as the electrode materials in rechargeable lithium-ion and sodium-ion batteries, as both anodes and cathodes, but the specific capacity, cost of manufacture, coulombic efficiency and cycling stability need to be improved before they can be used in practice.⁷⁴ MOFs have been further investigated as components of battery separators, used to segregate the anodic and cathodic regions of the cell,^{75,76} and as electrolytes either as pristine solid MOFs, or MOFs filled with ionic liquids.⁷⁷ As solid-state electrolytes or electrolyte additives, MOFs can prevent the unsafe formation of dendrites, whilst their high cation hopping site density can result in reduced activation energy for ionic conductivity.⁷⁸ It is anticipated that future work in this area will focus on understanding the role of grain boundaries and morphology on ionic conductivity and dendrite formation, as well as new methods of MOF fabrication to remove grain boundaries.⁷⁸

The final key application of MOFs to be considered is that of gas sensing. As this is of most relevance to this thesis, it will be covered in the following section dedicated solely to this application.

2.2 MOF gas sensors

As the demand for sensitive, selective and stable gas sensors has grown, MOFs have received a lot of interest as gas sensing media. Their unprecedentedly high surface area to volume ratio gives them an advantage in terms of both active sites per mass of material and adsorption capacity, which should enable high sensitivities to be accessed.⁷⁹ There is also potential to generate highly selective sensors with MOFs. By manipulating the pore dimensions through ligand extension, gaseous molecules can be excluded based on their size. Ligand and metal combinations can be selected to manipulate the electron density and distribution, hydrophobicity and acidity of the MOF environment to attract desired analytes.⁸⁰ Additional selectivity can be afforded through selection of ligands with functional groups that do not participate in bonding to the metal centres, leaving them free to interact with specific analyte guests.⁸¹ Another route is to use post-synthetic modification strategies to tailor internal functionality and consequent selectivity for a particular class of guests.⁸¹ There is also the potential for MOFs to be combined into a sensing array, in which the individual components respond slightly differently to different analytes. If enough components are combined, this should enable a characteristic pattern of responses to be generated for different analytes, enabling highly selective sensors to be fabricated.⁸² MOFs are also considered to be advantageous in their frequent ability to reversibly adsorb and release gases, requiring less energy to release their guests than zeolites.⁸⁰

As the preferred systems for gas sensing move away from spectroscopic techniques such as desktop mass-spectrometers, to smaller and cheaper systems such as handheld colorimetric devices, gas sensors that respond via a measurable change in a material's properties have become more commonplace. Gas sensors reliant on spectroscopic techniques, such as infrared spectroscopy, mass spectrometry or ion-mobility spectrometry, use machinery to record how

a continuous variable changes over a range, followed by substance identification through comparison with a known spectrum. Whilst accurate, these spectroscopic methods suffer from the need for a pre-concentration step² and are typically bulky, expensive and do not facilitate high sensitivity continuous stand-off monitoring of an environment.³ Instead, a number of materials that show measurable changes in properties on exposure to specific gases have been investigated. These include metal oxides, conducting polymers, carbon-based materials and MOFs.⁸⁰ In this section, gas sensors made from MOFs that detect gaseous analytes through a measurable change in a material property will be explored. They have been grouped in accordance with the property change that the analyte gas induces; optical, electronic and mechanical.

2.2.1 Optical MOF sensors

Most MOF-based optical gas sensors centre around detecting changes in refractive index triggered by particular analyte gases infiltrating the MOF pores. The first example of this was published in 2010 by Lu et al. who describe synthesising the 3D Zn-based MOF ZIF-8 as 1000 nm thick films on Si slides. As the thickness of the MOF film is of the order of magnitude of the wavelength of visible light, Fabry-Pérot interference peaks can be observed in UV-vis transmission spectra of the MOF films. On uptake of analyte gases into the MOF pores, the refractive index of the MOF changed and the peaks were observed to shift, with the magnitude of the shift correlating with the partial pressure of the analyte.⁸³ Shifts were observed when the MOF was exposed to gases including propane, n-hexane and ethanol, but no change was seen on exposure to water vapour or cyclohexane.⁸³ For a 1 nm resolution spectrophotometer, the detection limit for ethanol in water vapour was approximately 100 ppm.

A significant development to this technology has since been published by Hinterholzinger et al. who report layering ZIF-8 thin films with mesoporous TiO₂ layers to produce a 1D photonic crystal called a Bragg stack.⁸⁴ The rationale was that the red-shift of the Fabry-Pérot interference peaks would be amplified due to the significant refractive index contrast between the layer components and the increased number of layers. The sensor was found to respond to ethanol, methanol and isobutanol, but concentration vs response data was not obtained.⁸⁴ Further experiments by the same group involved forming additional Bragg stacks with HKUST-1 and CAU-1-NH₂ MOFs, then combining these with the ZIF-8 Bragg stack to produce a 3 component sensing array. By analysing the changes in wavelength on exposure to set concentrations of ethanol and methanol using principal component analysis, ethanol and methanol vapours could be distinguished.⁸⁵

Similar principles have been applied by researchers coating optical fibres with MOFs. Light from an LED travels through the MOF-coated fibre to a detector, where changes in transmission as a result of changed MOF refractive index altering the amount of light reflected back into the fibre can be measured, Figure 2.9.⁸⁶ It has been reported that the sensitivity of such devices should be higher than the Fabry-Pérot devices described above, due to the increased time the light waves spend propagating through the MOF.⁸⁰ Sensors to detect water vapour,⁸⁷ carbon dioxide^{88,86} and ethanol⁸⁹ have been fabricated with MOF-coated optical fibres.

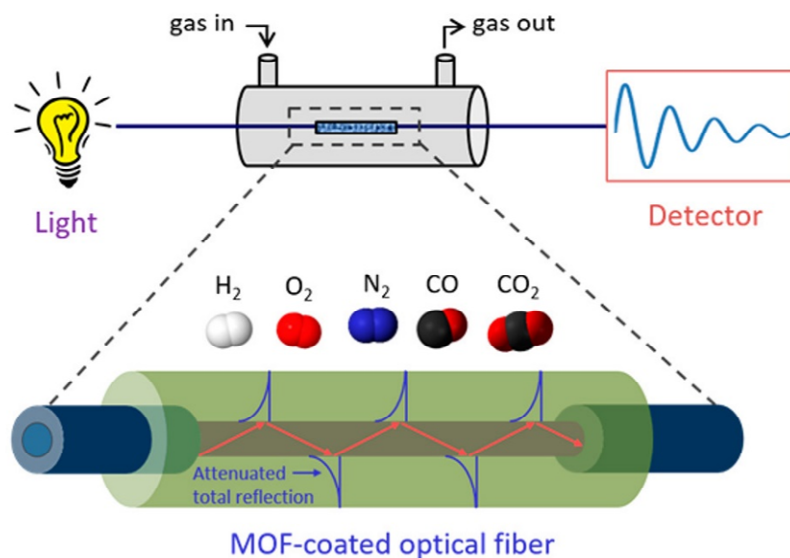


Figure 2.9: Schematic representation of a gas sensor made from a MOF-coated optical fibre. Adsorption of analyte gases into the MOF coating cause its refractive index to change, which affects the amount of light reflected back into the fibre resulting in a measurable change in % light transmission. Reproduced from reference 86.

MOFs have also been incorporated into surface plasmon resonance gas sensors. At metal surfaces there exist charge density waves known as surface plasmons.⁹⁰ When illuminated with a light source, a minimum in reflected intensity is observed at the incident angle which results in the parallel wave components of the incident light and the surface plasmon being equal.⁹⁰ The angle at which this intensity minimum occurs is sensitive to the refractive index of the environment above the film, which is in turn affected by the adsorption of gaseous analytes. Therefore, by monitoring the change in angle at which the intensity minimum occurs, the presence of gaseous analytes can be probed.⁹⁰ The first reports of SPR gas sensors use plasmonic nanoparticles such as Ag, Au and Cu to detect biomolecules, but more recent reports show that functionalising the nanoparticles with MOFs can enable volatile organic compounds, VOCs, to be detected.⁹¹ Vandezande et al. for example deposited ZIF-8 and ZIF-93 MOFs on Au SPR sensing layers and assessed their abilities to detect alcohol vapours, Figure 2.10.⁹² The ZIF-8 coated Au sensor was able to detect 2.5 ppm of methanol vapour, whilst the same sensor without any MOF showed no response.⁹²

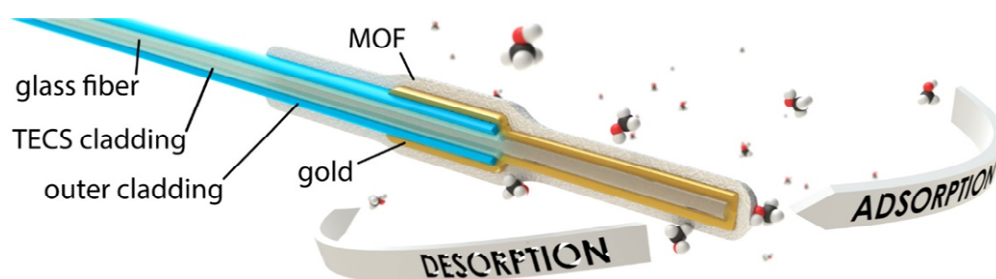


Figure 2.10: Schematic representation of the surface plasmon resonance gas sensor probe made by Vandezande et al. ZIF-8 and ZIF-93 MOFs are coated onto a layer of Au surrounding an optical fibre. Adsorption of analyte gases into the MOF coating causes its refractive index to change, which affects the surface plasmons in the Au layer. This is detected by a change in the measured surface plasmon resonance wavelength. Reproduced from reference 92.

Other optical gas sensors function by monitoring the quenching or enhancement of MOF luminescence on exposure to analytes. Luminescence in MOFs can be as a result of photo-responsive metal centres such as some lanthanides, emission from conjugated ligands, charge transfer between the metal and ligand, or emissions due to guest molecules.⁹¹ Among the successful luminescence enhancement gas sensors is the reported use of a Cu_4I_4 and pyridylphosphine-based MOF in detecting chlorinated volatile organic compounds.⁹³ Contrastingly, gas sensors based on fluorescence quenching include Eu-based MOFs able to detect nitro-aromatic explosives⁹⁴ and Zr-based porphyrinic MOFs able to detect oxygen.⁹⁵ As with most of the optical techniques however, detection of analyte presence with luminescent MOF sensors is via a shift of wavelength or intensity change. This typically requires laboratory equipment and substantial electronics to analyse, which needs to be addressed to further the applicability of these instruments.⁹¹

2.2.2 Mechanical MOF sensors

The subtle changes in mass or surface stress on adsorption of analyte gases have been used to generate a number of different sensing devices. These include microcantilevers, quartz crystal

microbalances, QCM, and surface acoustic wave, SAW, sensors. Functionalisation of devices of all 3 types with MOFs have been reported in literature. Microcantilevers translate surface stresses induced by analyte adsorption into a measurable response such as a change in deflection amplitude or resonant oscillation frequency.⁹⁶ A schematic representation of such a device is given in Figure 2.11.⁹⁷ MOFs can be used as the receptors to capture a number of gaseous molecules such as H₂O, CO₂ and CO gases.^{98,99} In particular, a sensor in which HKUST-1, Figure 2.4,¹⁸ was printed onto a microcantilever was able to detect *p*-xylene gas at a concentration of 400 ppb, which is lower than the 470 ppb that can be detected with the human olfactory system.¹⁰⁰

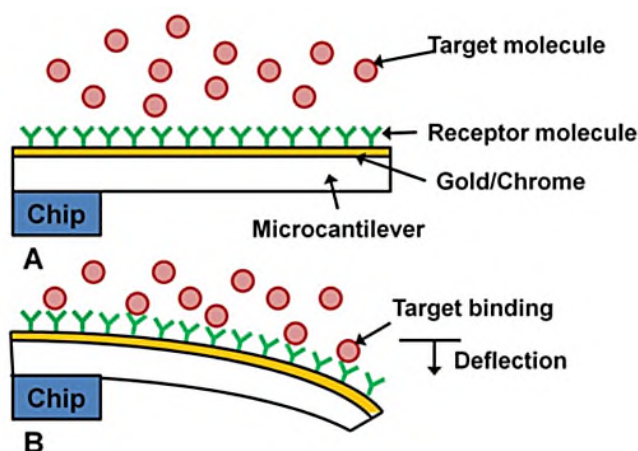


Figure 2.11: Schematic representation of microcantilever deflection on analyte adsorption. This can be adapted for non-biological systems by replacing the ‘receptor molecules’ with MOF layers able to capture VOCs. Binding of analyte gases to the surface induces stresses which result in a measurable change in deflection amplitude. Reprinted from reference 97.

QCM gas sensors work in much a similar fashion to microcantilevers. They typically consist of a quartz layer sandwiched between two electrodes. Changes in mass of the electrodes can be detected through changes in the resonant oscillation frequency of the device.¹⁰¹ By depositing MOF onto the electrodes, a variety of VOCs can again be captured and the resonant frequency shift measured. Investigations by Kitagawa et al. found that Cu₃(BTC)₂ MOF-functionalised QCM devices responded to hexane and methanol vapours, but that the size of

the MOF crystals had a greater impact on the frequency change than the type of analyte vapour.¹⁰² Fischer et al. subsequently employed oriented $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ MOF films in QCM devices and found that the performance of the sensor for detection of VOCs such as benzene, toluene and p-xylene was highly dependent on the orientation of the MOF crystals.¹⁰³

Surface acoustic wave, SAW, sensors detect analytes through monitoring changes in resonant frequency or phase shift of an acoustic wave travelling through a piezoelectric material.¹⁰⁴ A voltage is applied across electrodes on the piezoelectric, this generates acoustic waves that propagate across the surface and are reflected off gratings to enable resonance.¹⁰⁵ The resonant frequencies obtainable are higher than those reached in QCM and microcantilever techniques, which, as proven experimentally by Dickert et al.,¹⁰⁶ offers superior sensitivity.¹⁰⁵ Adding MOFs into the path of the acoustic wave propagation has enabled CO_2 , CH_4 , acetone, ethanol and NH_3 to be detected.⁸⁰ One of the most sensitive MOF-based SAW sensors published to date, is one made from the Zn-based MOF, MFU-4. This device was able to detect CO_2 , H_2 , He, NH_3 and H_2O gases, with CO_2 concentrations of 1 ppmv still giving a measurable response.¹⁰⁷

2.2.3 Electronic MOF sensors

MOFs can be utilised to make sensing devices that respond to analyte gases through changes in their electrical properties such as resistance, capacitance or work function. Capacitive or impedimetric gas sensors can be made by inserting an insulating MOF between two conductive electrodes and applying an alternating current. The permittivity, impedance or dielectric constant of the MOF can then be monitored when exposed to gaseous analytes. The first major works in this area were performed by Achmann et al. who synthesised Al-

teraphthalate, Cu-1,3,5-benzenetricarboxylate (Cu-BTC), Fe-1,3,5-benzenetricarboxylate (Fe-BTC) and two further sensing media by doping samples of the Fe MOF with Li and Fe(II). Sensors were made by screen-printing a MOF paste onto IDEs and applying heat to evaporate the organic component of the paste and leave a thick MOF film, or by trapping a MOF pellet between metal disc electrodes as in Figure 2.12.¹⁰⁸ The sensors were exposed to samples of H₂, NO, CO₂, C₃H₈, H₂O, methanol and ethanol vapours and impedance spectrometry was used to monitor changes in the electronic environments of the MOFs on exposure to different concentrations. Of those tested, only ethanol, methanol and H₂O exposure resulted in a decrease in impedance of the undoped Fe MOF.¹⁰⁸ The magnitude of impedance change was however far lower for ethanol and methanol than it was for comparable concentrations of water, and as such the only potential application was humidity sensing. Whilst the sensors could not compete with humidity sensors already available, the concept of MOF deposition onto IDEs to produce sensors is something that has been performed in the field ever since.

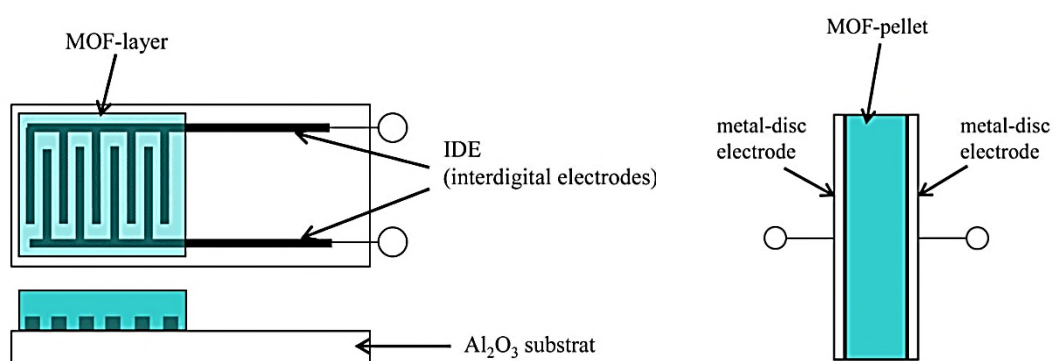


Figure 2.12: Diagrams to illustrate the format of impedance sensors made using (a) deposition of MOF onto inter-digitated electrodes and (b) MOF pellets. In both cases conductive MOF bridges gaps between metal electrodes. Similar set-ups have been used to integrate MOFs into electrical devices ever since. Reproduced from reference 108.

Significant progress has since been made by Eddaoudi et al. who synthesised a MOF from Yttrium and fumaric acid and then used it to fabricate a capacitive inter-digitated electrode

sensor. The sensor was able to selectively detect H₂S gas against CH₄, NO₂, H₂ and C₇H₈. A linear relationship between change in capacitance and H₂S concentration was obtained, and from this a limit of detection of 5.4 ppb was calculated.¹⁰⁹ In 2021 Zhao et al. synthesised NUS-8 MOF from zirconium chloride and conjugated phenyl-group based ligands with –NH₂, –CH₃ or –H functional groups, and compared the performance of the 3 MOFs in capacitive sensors. They found that the –NH₂ functionalised MOF sensor was the most sensitive to acetone vapour, although concentrations below 75 ppm were not tested.¹¹⁰

The use of MOFs as active materials in field effect transistors, FETs, has been explored to a lesser extent than capacitive sensors. Such sensors work by transducing shifts in work functions of a sensing medium, initiated by adsorption of analytes, to changes in drain current measured between the source and gate electrodes. There are a number of reports of such devices being made using both polymers and MOFs together. Ameloot et al. report using a kelvin probe device with UiO-66-NH₂ MOF to detect dimethyl methylphosphonate (as a model for the nerve agent, sarin) with a calculated limit of detection of 2 ppb at 50 % humidity.¹¹¹ A schematic illustration of the kelvin probe set-up used can be seen in Figure 2.13.¹¹¹ Similarly, Davydovska et al. report that adding a Cu-BTC MOF layer onto a TiN electrode enabled aldehydes to be detected through changes in the work function.¹¹²

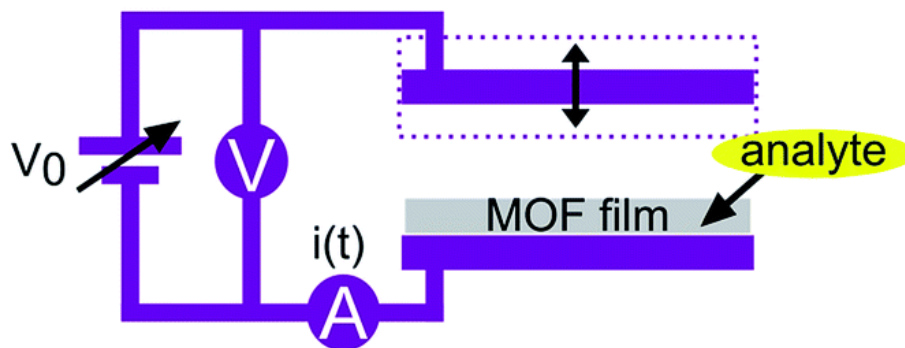


Figure 2.13: Schematic illustration of the kelvin probe gas sensor set-up used by Ameloot et al. to detect an analogue of the nerve agent sarin. The MOF is coated onto a stationary electrode which is connected to an oscillating reference electrode. As analyte is adsorbed by the MOF film, the chemical potential changes which changes the surface work function. A balancing potential is applied between the two electrodes, but as the work function changes, a potential difference between the electrodes arises and current flows. Reproduced from reference 111.

Sensors fabricated from conductive MOFs that respond to analyte adsorption through measurable changes in their resistance are a promising route to producing commercial gas sensors. These so-called chemiresistive sensors are the most pertinent to the experimental work in this thesis and will therefore be discussed within the next section which is dedicated to electrically conductive MOFs.

2.3 Electrically conductive MOFs

The majority of MOFs are electrical insulators, but since the first intrinsically conductive MOF was synthesised in 2009,¹¹³ the field has gained increasing amounts of attention. Enhancing the conductivity of MOFs is of interest to those looking to make chemiresistive sensors, electrocatalysts and charge storage devices.¹¹⁴ The conductivity of a material describes the ease with which charge carriers can be transported through it, with both the concentration of charge carriers and their mobility contributing to the conductivity value.¹¹⁵ Five different mechanisms of transporting charge through MOFs have been identified; through-bond, extended conjugation, through-space, redox hopping and guest-promoted

transport pathways. These are represented schematically in Figure 2.14 which has been reproduced from the 2020 publication by Xie et al.¹¹⁴ In this section these charge transport mechanisms will be explained, and key examples of MOFs using each mechanism will be discussed.

The section will conclude with a discussion of the structure and conductivity of the class of MOFs focused on in this thesis.

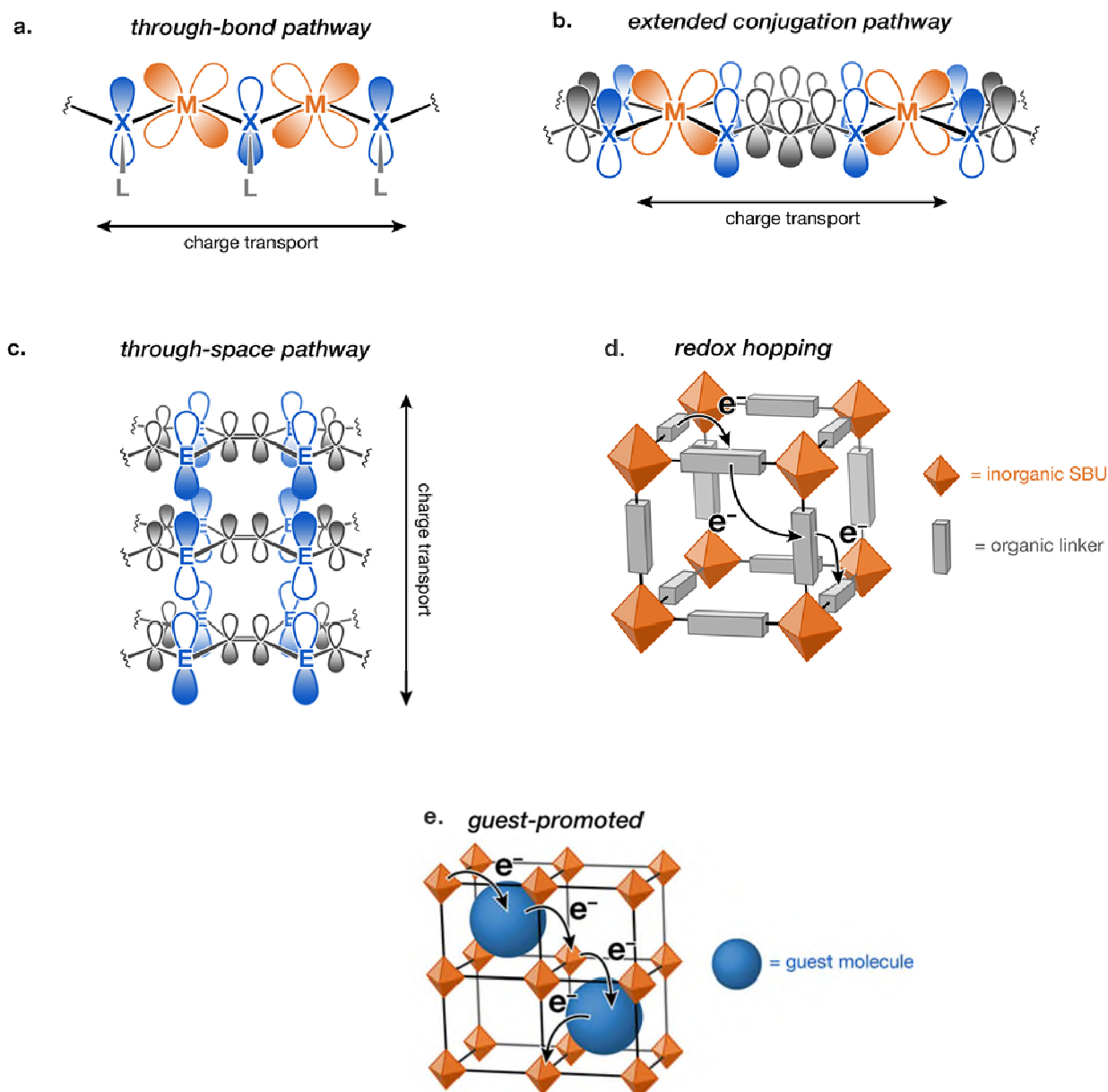


Figure 2.14: Diagrams to represent the possible charge transfer mechanisms taking place in a MOF. **(a) – (c)** Linker heteroatom orbitals are shown in blue, metal orbitals are shown in orange and linker backbone orbitals are shown in grey. **(a)** Through-bond transport due to overlap of metal and linker orbitals. **(b)** An example extended conjugation transport pathway formed from overlapping metal d-orbitals and linker p-orbitals. **(c)** Through-space transport pathway due to π - π stacking of out-of-plane linker orbitals. **(d)** Electron transport via redox hopping between organic linkers. **(e)** Electron transport from metal SBU to guest molecules. Figure is reproduced and modified from reference 114.

2.3.1 Through-bond charge transport

For frameworks where there is good energetic and spatial overlap between the linker and metal SBU orbitals, a continuous covalent pathway for charge to flow through the structure can exist. Such MOFs are said to transfer charge via a through-bond pathway.¹¹⁴ Good energetic and spatial overlap of the metal SBU and ligand orbitals is needed for the band gap to be low enough for the charges to hop from the metal to the linker groups, increasing the charge mobility. Such a situation is quite rare for 3D MOFs which don't also contain extended conjugated regions. Successful synthesis of 3D MOFs reliant on through-bond charge transfer mechanisms typically involve softer and less electronegative ligand groups, to reduce the ionic character of the bond and so improve the spatial and energetic overlap between the SBUs.

An important study in this area was carried out by Sun et al. in 2017.¹¹⁶ They synthesised MOFs from Mg, Mn, Fe, Co, Ni, Cu and Zn metal centres with 2,5-dihydroxybenzene-1,4-dicarboxylic acid linkers. The conductivity of the resulting MOFs was found to be increased by roughly one order of magnitude by substitution of the hydroxyl groups on the ligand for thiol groups, resulting in the metals coordinating to the softer sulphur groups on the ligand. The highest reported conductivity for the MOFs formed in this experiment was that of the Fe and thiol-functionalised MOF, with a value of $3.9 \times 10^{-6} \text{ S cm}^{-1}$.¹¹⁶ Other MOFs reliant on through-bond charge transport for their conductivity often include azolate-based linkers. One of the highest reported conductivities for such an azolate MOF is that of the Fe(1,2,3-triazolate)₂ MOF which has a conductivity of $7.7 \times 10^{-5} \text{ S cm}^{-1}$.¹¹⁷

2.3.2 Extended conjugation

When transition metal ions are bonded to ligands via groups that are conjugated with the rest of the ligand, the conjugation can be extended throughout the MOF.¹¹⁴ For this to be possible, the ligand itself must be fully conjugated, and the metal must have a d-orbital in the correct orientation for overlap with the organic linker plane to allow for π -d conjugation. Many MOFs with extended conjugation planes are made up of 2D sheets that stack to form 3D structures, with high conductivities within the 2D layers. This is exemplified in the coronene-based framework synthesised by Dong et al., Figure 2.15, which has a remarkable conductivity of 10 S cm^{-1} at 300 K.¹¹⁸

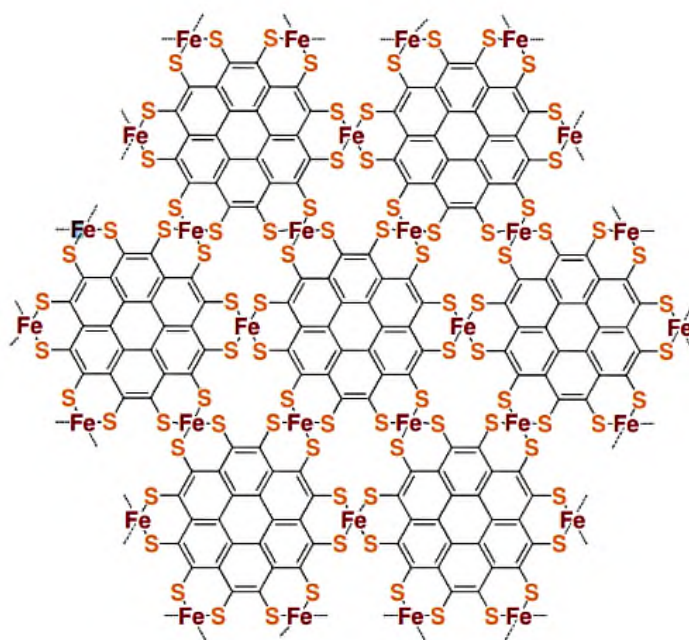


Figure 2.15: Schematic representation of the square planar Fe 1,2,3,4,5,6,7,8,9,10,11,12 – perthiolated coronene 2D MOF. Full π -d conjugation throughout the plane leads to exceptional conductivity. Reproduced from reference 118.

Success has been reported in synthesising 2D MOFs with extended conjugation using a variety of organic linkers.¹¹⁹ These include hexa-substituted triphenylenes,¹²⁰ hexa-substituted benzenes¹²¹ and pyrenetetraone ligands.¹²² When used to make MOFs through solvothermal

synthesis, these molecules typically undergo partial oxidation and deprotonation in order to facilitate bonding to the metal SBUs. This can lead to higher charge carrier densities in the resulting MOF which can be favourable for the conductivity.¹²¹ Whilst conductivity is conferred through extended conjugation in the *ab* plane, conductivity in the third dimension arises through π - π interlayer interactions.

3D MOFs with extended conjugation are much rarer, but have been reported for MOFs made from dihydroxybenzoquinone molecules with some transition¹²³ and rare-earth metals.¹²⁴ The MOF made from Fe and dihydroxybenzoquinone, $[\text{Fe}_2(\text{dhbq})_3]^{2-}$, is formed from two independent enantiomeric interpenetrated nets and was measured to have a high conductivity of 0.16 S cm^{-1} . However, bulky tetrabutylammonium ions were required to stabilise the charge, occupying the pores and reducing the usable porosity of the framework.¹²⁵

2.3.3 Through-space charge transport

MOFs with conjugated ligands can participate in π - π interactions with conjugated systems on other ligands if correctly oriented relative to each other. This is common for 2D conductive MOFs that form flat layers and stack to enable favourable interactions between aromatic systems. This introduces a charge transport pathway across the layers as depicted in Figure 2.14 (c). It is accepted that the charge mobility decreases as the spatial separation of the interacting π systems increases.¹²⁶ A study by Xie et al. synthesised MOFs consisting of La^{3+} ions and tetrathiafulvalene tetrabenzoate, TTFTB, ligands under different synthesis conditions.¹²⁷ This led to MOFs with different stacking motifs. Conductivity measurements revealed that the larger the distance between the centre of the ligands, the lower the measured conductivity. These MOFs are uniquely suitable for this study as they contain conjugated ligands that can facilitate π - π interactions, but do not have an extended metal-ligand

conjugation pathway. This means that the through-space contribution to the conductivity can be studied in isolation. Another 3D MOF synthesised from Cd^{2+} ions and N,N'-di(4-pyridyl)-1,4,5,8-naphthalenetetracarboxdiimide ligands reached conductivities of $3.3 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature.¹²⁸ The shape of the ligand in this MOF is such that full conjugation within the ligand is not possible, which means that the π - π interactions are solely responsible for the measured conductivity.

For 2D layered MOFs with extended conjugation in the *ab* plane, the extent of the contribution of the π - π interactions to the measured conductivity is not fully understood.¹¹⁴ Unless the conductivity across a single crystal of the MOF in question can be measured, the effect of the grain boundaries on the measured conductivity further complicates the picture.

2.3.4 Redox hopping

For MOFs in which the conditions for through-bond, through-space and extended conjugation charge transport are not met, any measurable conductivity of a MOF with vacant pores can be assumed to be down to redox hopping. This is the case for MOFs that do not contain π systems that can interact favourably through space, or any redox-active components close enough for orbital overlap to occur.¹¹⁴ Redox hopping involves charge transfer within the MOF from metal to metal group, and/or from linker to linker group, or metal to linker.

MOFs reliant on redox hopping between linkers for their conductivity include $\text{Zr}_6\text{O}_4(\text{OH})_8(\text{Me}_2\text{BPDC})_4$ and $\text{Zn}_4\text{O}(\text{NDC})_3$, with reported conductivities of 1.3×10^{-5} and 0.04 S cm^{-1} respectively.^{129,130} The conductivity of 0.04 S cm^{-1} for the $\text{Zn}_4\text{O}(\text{NDC})_3$ MOF synthesised from zinc acetate and 2,6-naphthalene dicarboxylic acid, is orders of magnitude higher than the conductivities reported for other MOFs with only redox hopping transport mechanisms.¹¹⁴ The authors rationalised this in terms of the interpenetrated MOF structure

allowing for efficient charge hopping between the naphthalene ligand cores.¹³⁰ In addition to the groups being spatially close enough to facilitate hopping, the redox centres should have similar reduction potentials. For metal-metal or ligand-ligand hopping the potential requirement is not an issue, but for metal-ligand hopping to occur the difference in reduction potential can be the conductivity-limiting factor. Ahrenholtz et al. synthesised the MOF CoPIZA from Co(III) tetracarboxyphenylporphyrin and Co(II) carboxylate SBUs.¹³¹ Analysis of the MOF using cyclic voltammetry and spectroelectrochemical techniques found the reduction of the ligand-containing SBUs and metal containing SBUs to occur within 0.2 V of each other. Redox hopping was concluded to be occurring through analysis of experimentally obtained diffusion parameters and further spectroelectrochemical measurements.¹³¹

2.3.5 Guest-promoted charge transport

Some insulating MOFs can be made conductive by encapsulating electroactive guests. These guest species can facilitate electron transport from guest to guest, or from framework to guest, as depicted in Figure 2.14 (e).¹¹⁴ A number of different types of guest have been found to increase the conductivity of MOFs, these include; iodine and polyiodides,¹³² organic molecules such as tetracyanoquinodimethane,¹³³ organometallics such as ferrocene¹³⁴ and conductive polymers.¹³⁵ Of particular note is the work by Hu et al. who reported a 10^7 times increase in conductivity when I₂ was adsorbed by the Cu and Tb heterometallic isonicotinate MOF, [Tb(Cu₄I₄)(ina)₃(DMF)].¹³⁶ Comparison of the single crystal structure before and after I₂ uptake revealed that the I₂ molecules were successfully bridging the Cu₄I₄ groups across the pores through I...I₂...I interactions, as depicted in Figure 2.16.¹³⁶ Whilst strategies such as this are often successful in introducing conductivity, it comes at the cost of reducing the

available pore volume of the MOF, which is undesirable for a number of common MOF applications.¹¹⁴

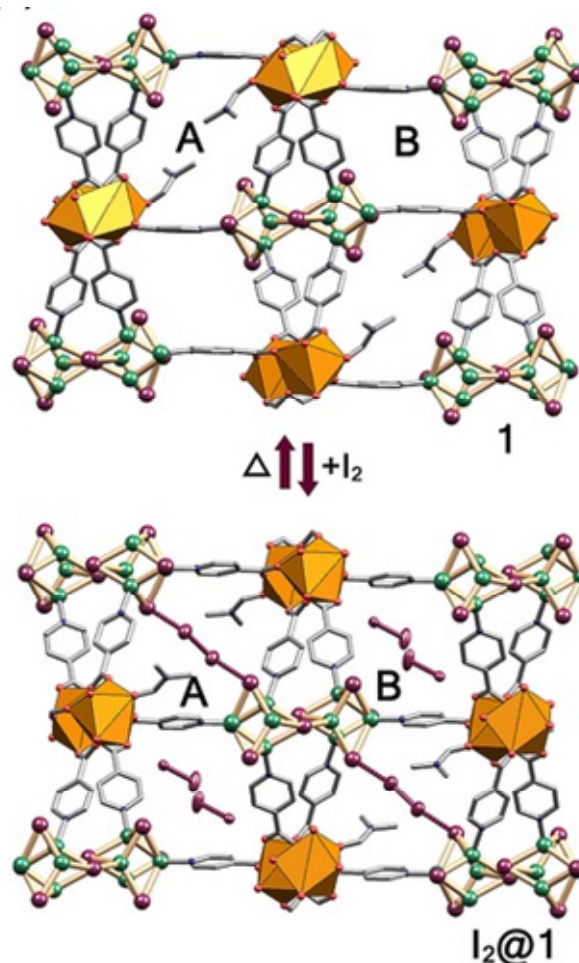


Figure 2.16: The crystal structure of the heterometallic isonicotinate MOF, [Tb(Cu₄I₄)(ina)₃(DMF)] before I₂ loading (**top**) and after I₂ loading (**bottom**). I₂ molecules bridge between Cu₄I₄ groups to increase the conductivity of the framework by a factor of 10⁷. **Key:** Cu (green), I (purple), O (red), C (grey). The Tb³⁺ polyhedral are shaded in yellow. Reproduced from reference 136.

2.4 Hexa-substituted triphenylene MOFs

MOFs based on hexa-substituted triphenylene ligands, HXTP ligands, have attracted a lot of attention because of their good conductivities and potential applications in electronics.¹²⁰ It is MOFs in this family that are synthesised and used as sensors in this thesis. Their structure, synthesis routes, and chemiresistive sensing behaviour will be explored in the remainder of this chapter.

2.4.1 Structure and conductivity

The MOFs in the HXTP family are comprised of single ion metal centres joined by HXTP-based linkers to form hexagonal sheets. Three different molecules are used as the starting materials to form MOFs in this family; 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP), 2,3,6,7,10,11-hexaaminotriphenylene (HATP) and 2,3,6,7,10,11-hexathioltriphenylene (HTTP). These molecules are depicted in Figure 2.17.

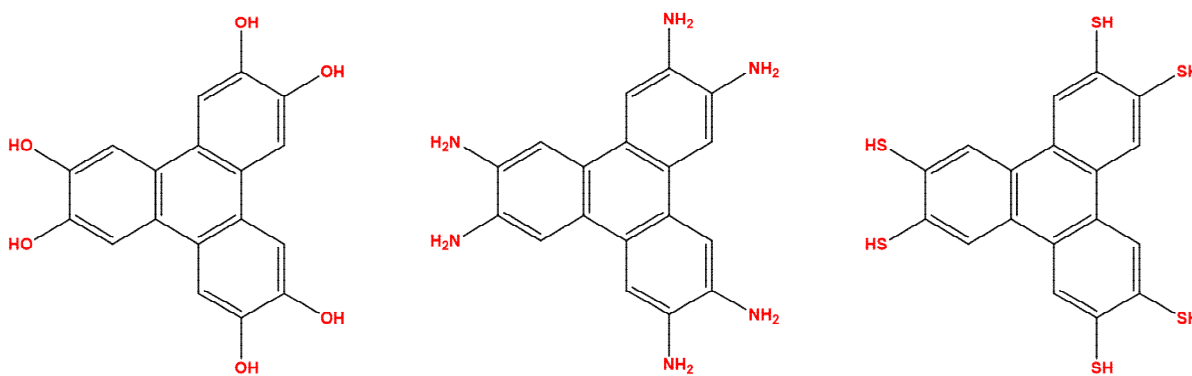


Figure 2.17: Molecular structures of the three molecules used to form linkers in the hexa-substituted triphenylene MOF family. **Left** - 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP), **Centre** - 2,3,6,7,10,11-hexaaminotriphenylene (HATP), **Right** - 2,3,6,7,10,11-hexathioltriphenylene (HTTP).

In order to coordinate to metal ions and form 2D hexagonal layers, the ligands must be activated to their anionic and partially oxidised states. Each ligand can exist in oxidation states between 0 and -6, depending on the extent of oxidation and deprotonation. MOFs in this family are known to contain metal and organic linker species in a 3:2 ratio, forming MOFs with general formulas of $M_3(\text{HXTTP})_2$. The metal ions used are typically $2+$, which means that a linker charge of $3-$ is required to maintain charge neutrality. Such linker species with a $3-$ charge are formed when the hetero groups on the starting molecules are deprotonated, and then partially oxidised through losing 1 electron per functional group pair. This process is depicted for a single functionalised phenyl group in Figure 2.18.¹³⁷ On the left of this figure is the deprotonated molecular starting material with an oxidation state of $2-$. Loss of 1 electron to form a $1-$ oxidation state group produces the radical species in the centre of the figure. If this happens on each of the phenyl groups in the hexa-substituted triphenylene molecule, a $3-$ charged species is formed. This can then coordinate to M^{2+} ions to form hexagonal MOF sheets conforming to the $M_3(\text{HXTTP})_2$ MOF formula.

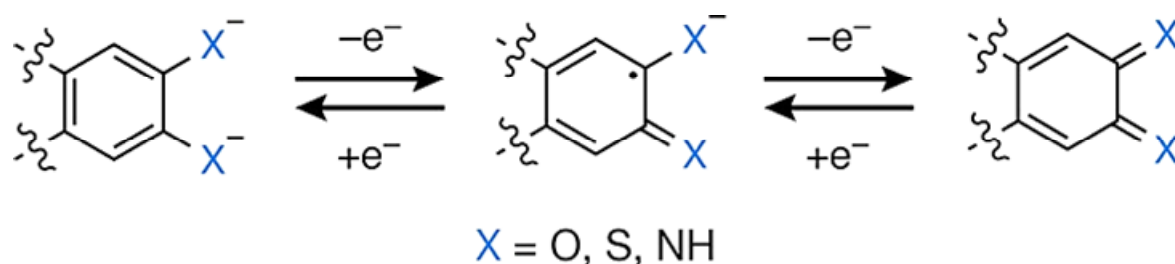


Figure 2.18: Redox structures of the $2-$, $1-$ and 0 charge states for a deprotonated fragment of a hexa-substituted triphenylene molecule. Deprotonation followed by partial oxidation produces the radical species in the centre of the figure. This species can then coordinate to M^{2+} ions to form 2D MOF sheets with extended conjugation. Reproduced from reference 137.

Whilst most of the MOFs in the HXTTP family contain semi-oxidised linker groups analogous to the one depicted in the centre of Figure 2.18, metal centres with flexible valency can support linker groups with different oxidation states. This is most common for Cu-containing MOFs

in which there is evidence to indicate that both Cu^+ and Cu^{2+} ions are present. Redox communication between the ligands and metal centres has implications for the chemiresistive sensing behaviour of the MOFs and will be discussed in more detail in section 2.5.

The structure of a single 2D MOF sheet is depicted in Figure 2.19. The metal centres, M, can be Cu^{2+} , Ni^{2+} , Co^{2+} or Pt^{2+} ions. If the functionality of the linker is $-\text{O}$, the linker is termed HHTP for hexahydroxytriphenylene, if it is $-\text{NH}$ it is termed HTP for hexaiminotriphenylene, and if it is $-\text{S}$ it is termed HTTP for hexathioltriphenylene.

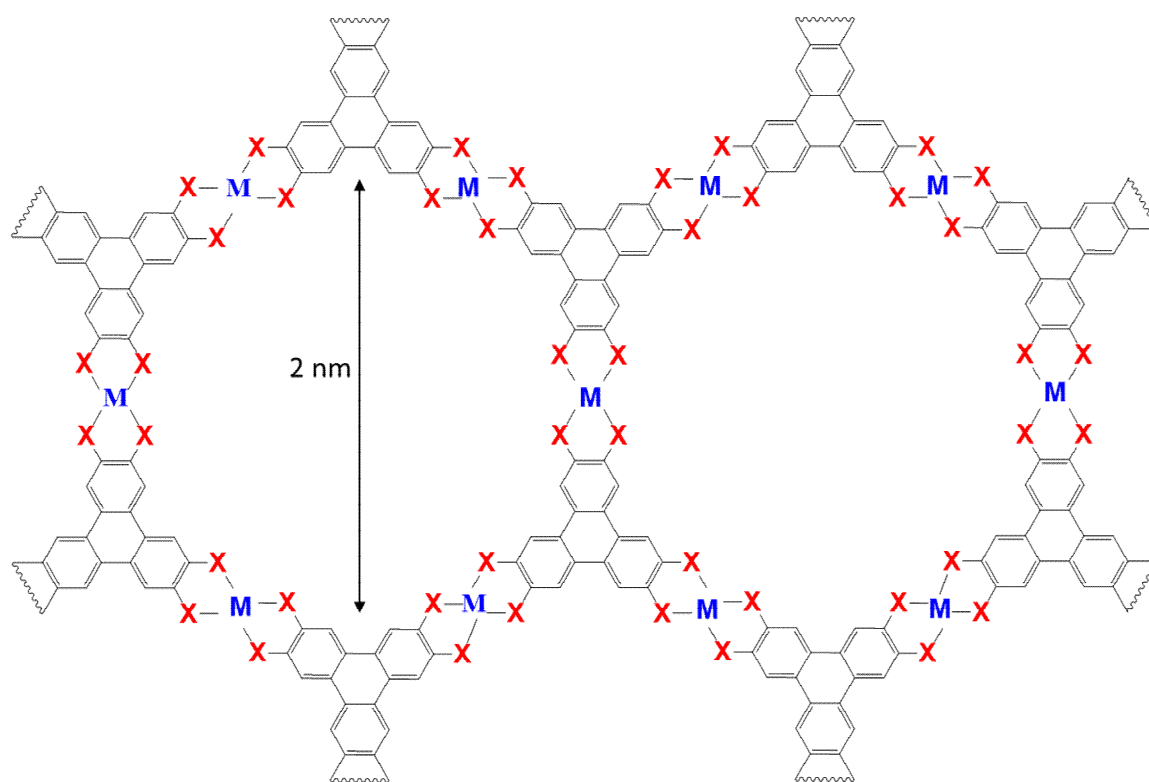


Figure 2.19: Structure of a single 2D layer of hexa-substituted triphenylene-based MOFs. M can be Cu^{2+} , Ni^{2+} , Co^{2+} or Pt^{2+} ions. If $X = \text{O}$, a $\text{M}_3(\text{HHTP})_2$ MOF is formed. If $X = \text{NH}$, an $\text{M}_3(\text{HTP})_2$ MOF is formed. If $X = \text{S}$, an $\text{M}_3(\text{HTTP})_2$ MOF is formed. At the widest point, the pore diameters are approximately 2 nm.

The same planar hexagonal structure is formed for all of the metal and ligand combinations but the way in which these layers stack varies to give different 3D structures. The reported

stacking modes of MOFs of this family are slipped parallel AAAA, eclipsed AAAA, staggered AAAA, or interpolated ABAB, where A layers have identical in-plane structures as depicted in Figure 2.20 and B layers have a different arrangement of metal and ligand groups. Most of these structures were obtained through a combination of powder X-ray diffraction and computational analysis.^{138,139,140} Only the structure of $\text{Co}_3(\text{HHTP})_2$ has been obtained with single crystal X-ray diffraction,¹⁴¹ but in 2021 the structures of single crystals of $\text{Ni}_3(\text{HITP})_2$ and $\text{Cu}_3(\text{HHTP})_2$ were probed using high resolution TEM.¹⁴² The stacking modes of the MOFs formed from the different metal and ligand combinations are depicted in Figure 2.20.¹²⁰ All of the structures involve stacking of complete hexagonal layers as drawn in Figure 2.20, apart from the interpolated structures exhibited by $\text{Co}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HHTP})_2$. In these structures the hexagonal sheets are alternated with ordered layers of discrete hydrated $\text{M}_3(\text{HHTP})$ units.¹⁴³

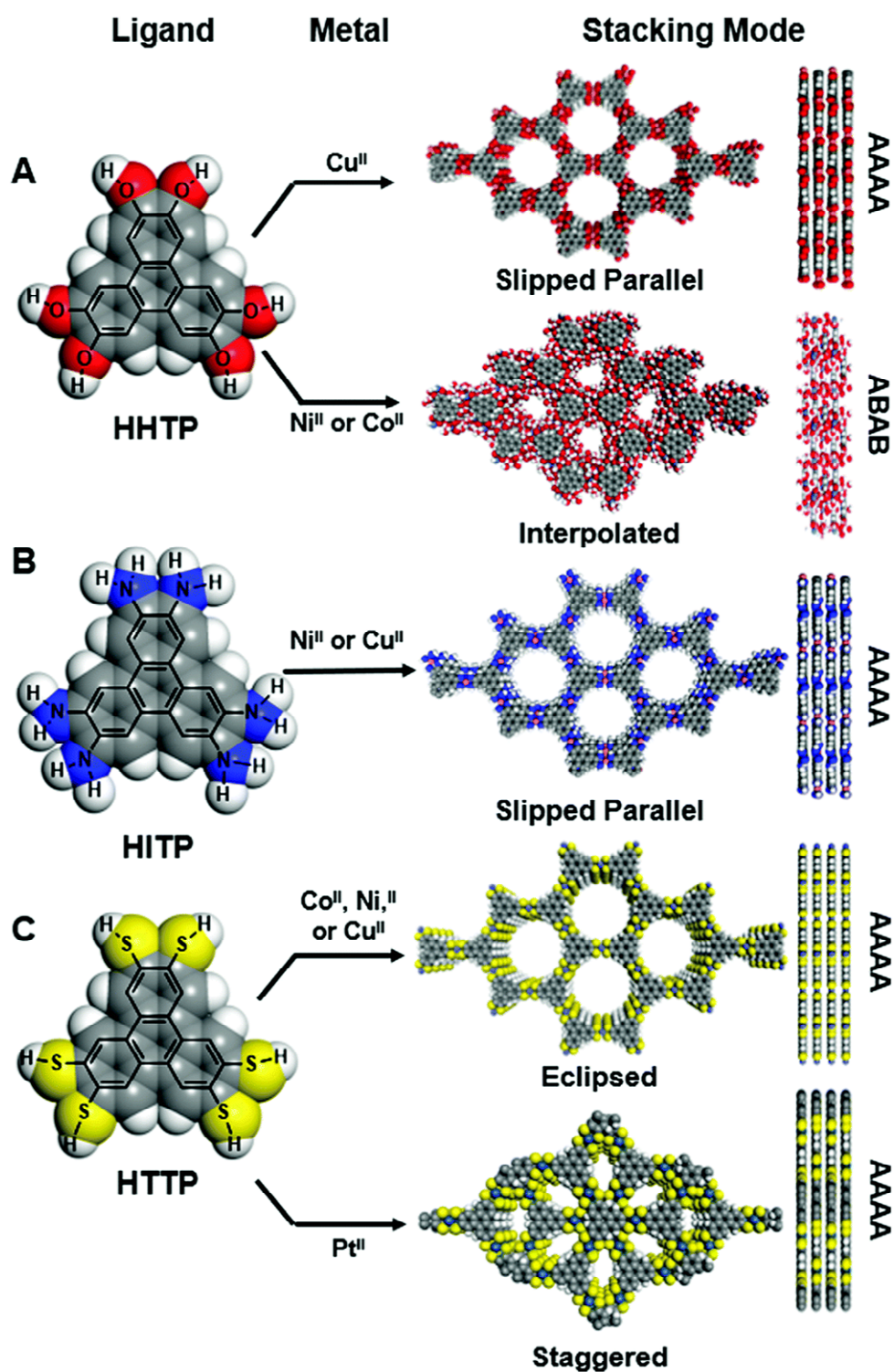


Figure 2.20: Schematic illustration of the stacking modes formed when Cu^{2+} , Ni^{2+} , Co^{2+} or Pt^{2+} metal ions are used to form MOFs with HHTP, HITP or HTTP linkers. The 2D layers stack to form MOFs with staggered AAAA, eclipsed AAAA, interpolated ABAB or slipped parallel AAAA stacking modes. Reproduced from reference 120.

MOFs in the HXTP family are conductive within the 2D sheets due to the extended conjugation facilitated by interactions of the metal out-of-plane d-orbitals with the π -system of the fully conjugated planar ligands. Conductivity perpendicular to the layer planes arises due to through-space charge transfer by way of π - π interactions. A study of the electronic structure of the $\text{Cu}_3(\text{HHTP})_2$ MOF by Rubio-Giménez et al. used dispersion corrected density functional theory, DFT, to look at the density of states near the Fermi level.¹⁴⁴ By projecting the density of states onto specific atoms, they found that the ligand C and O 2p orbitals made the largest contributions, which is suggestive of strong π - π interactions between the layers.¹⁴⁴ Studies on single crystals of HXTP MOFs are lacking, but in 2019 Day et al. found that the in-plane and out-of-plane conductivity of $\text{Cu}_3(\text{HHTP})_2$ rods were of comparable orders of magnitude.¹⁴²

There is some disagreement as to whether multi-layered HXTP MOFs should be considered to have metallic or semiconducting conductivity.¹²⁰ For example, reports by Dincă et al. found $\text{Ni}_3(\text{HITP})_2$ to act as a semiconductor,¹³⁹ whilst computational studies by Chen et al. found multi-layered $\text{Ni}_3(\text{HITP})_2$ and $\text{Cu}_3(\text{HITP})_2$ to have metallic conductivities.¹⁴⁵ DFT calculations by Rubio-Giménez et al. found $\text{Cu}_3(\text{HHTP})_2$ to be a semiconductor with a theoretical band gap of 0.33 eV,¹⁴⁴ compared to an experimental band gap of 0.48 eV.¹⁴⁶ Their calculations also found the band gap to increase as the interlayer separation increased, reaching 0.58 eV at an interlayer separation of 5.36 Å.¹⁴⁴ Potential reasons for the differences in measured and calculated band gaps were described by Foster et al. who postulate that transport barriers such as perpendicular grain boundaries that are not considered in theoretical calculations could be responsible for the discrepancies.¹⁴⁷

The semiconducting behaviour of $\text{Cu}_3(\text{HHTP})_2$ has been investigated in a number of studies. The first experiments based on ultraviolet photoelectron spectroscopy¹⁴⁸ and FET

measurements¹⁴⁶ concluded that $\text{Cu}_3(\text{HHTP})_2$ was a p-type semiconductor. Further work by Bradshaw et al. attributed the p-type behaviour to adsorbed H_2O or O_2 molecules at the metal sites of the MOF.¹⁴⁹ They used XPS and Seebeck measurements to compare two electrochemically-synthesised $\text{Cu}_3(\text{HHTP})_2$ samples, onto which polymer layers were drop-cast at different temperatures. The polymer layer was used to transfer the MOF from the metallic substrates on which they were synthesised to substrates suitable for analysis, after which the polymer was dissolved. XPS analysis found the sample dried at the lower temperature to have less oxygen than that dried at a higher temperature, whilst Seebeck measurements found the sample including more oxygen to behave as a p-type semiconductor whilst the other behaved as an n-type semiconductor. They therefore concluded that H_2O and O_2 were acting as p-type dopants to the MOF, and that semiconducting character of the MOF could be tuned by changing the drying conditions.¹⁴⁹

Studies on $\text{Ni}_3(\text{HITP})_2$ MOF samples have also reached different conclusions about its semiconducting behaviour. Thermoelectric studies on $\text{Ni}_3(\text{HITP})_2$ MOF pellets by Sun et al. indicate that it is n-type,¹⁵⁰ whilst similar experiments performed on a $\text{Ni}_3(\text{HITP})_2$ thin film showed the MOF to be a p-type semiconductor.¹⁵¹ From these experiments it can be concluded that the semiconducting behaviours of MOFs in the HXTP family are likely to be highly dependent on factors such as atmospheric dopants, solvents, sample thickness and drying conditions. This suggests that the way the MOF resistances respond to reducing and oxidising gases may vary significantly with the MOF synthesis method.

2.4.2 Synthesis methods and device integration

2D conductive MOFs based on HXTP ligands were first synthesised via solvothermal methods. This typically involves mixing solutions of the metal salt and ligand, heating the mixture and waiting for the MOF to form via self-assembly.¹²⁰ The MOF can then be washed and filtered, yielding it as a microcrystalline powder. For such MOF samples to be integrated into electronic devices, methods like drop-casting can be used. The MOF is first dispersed in a solvent, then pipetted onto the desired substrate. Whilst simple and quick, drop-cast MOF systems often suffer with inhomogeneous distribution of the MOF on the substrate, uneven thicknesses, aggregation of MOF particles, high inter-particle contact resistance and poor substrate adhesion. Other methods of integrating powdered MOF samples into functional devices include mechanical compression and abrasion. The MOF powder can be compressed into a mould in the shape of a pellet for example, or abraded onto the desired substrate. For example, Campbell et al. compressed $\text{Ni}_3(\text{HITP})_2$ MOF into small pellets that were then inserted into a mechanical pencil from which they could be drawn onto paper substrates.¹⁵² Similarly, Ko et al. report blending HXTP MOF powders with graphite, then drawing them onto paper with a pencil-like device.¹⁵³ Such methods are advantageous in that there is no opportunity for solvents to influence the MOF.

Even better are methods that synthesise the MOF in situ on the desired substrates, circumventing the need to deposit the MOF after synthesis. One such method is the spray layer-by-layer synthesis method reported by Yao et al. in which substrates are in-turn sprayed by solutions of ligand and metal salt to obtain the desired $\text{Cu}_3(\text{HHTP})_2$ MOF.¹⁴⁸ The steps of this process are outlined in Figure 2.21.¹⁴⁸ Success was achieved with silicon, quartz and sapphire substrates, but the piranha solution substrate functionalisation that was required rules out this method to obtain MOF on flexible substrates such as PET, paper and textiles.

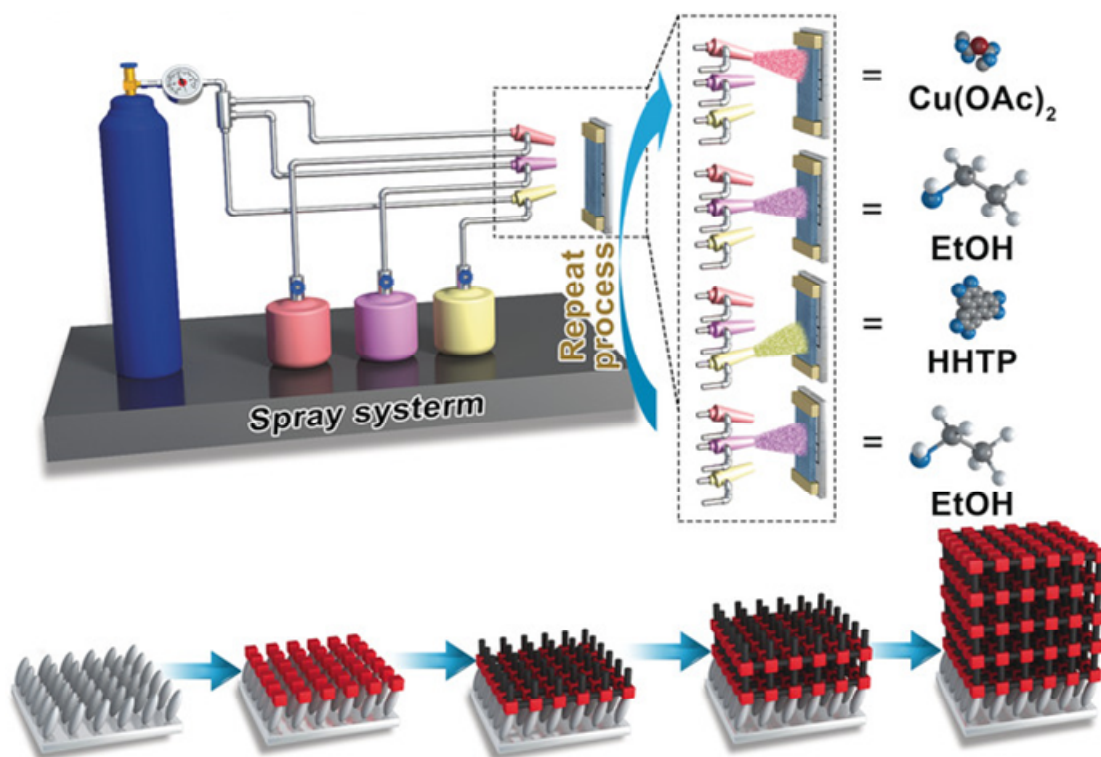


Figure 2.21: Schematic illustration of the steps performed to produce thin film $\text{Cu}_3(\text{HHTP})_2$ MOF sensors by spray layer-by-layer synthesis. The copper salt is first sprayed onto the substrate, followed by the ethanol solvent, then the HHTP ligand and then another layer of the ethanol solvent. These steps are repeated to form more layers of the MOF. Reproduced from reference 148.

A vapour-assisted conversion technique was explored by Mahringer et al. to synthesise 180 to 200 nm thick films of $\text{Ni}_3(\text{HHTP})_2$ and $\text{Co}_3(\text{HHTP})_2$ MOFs on quartz and conductive substrates.¹⁵⁴ They coated the desired substrate in a 1:2 ratio ligand/metal salt solution and then placed it on glass spacers above a mixture of water and isopropanol solvents in a sealed autoclave. This was then heated to 85 °C for a minimum of 3.5 hours, Figure 2.22. The result was orientated thin films of the MOFs, with the crystal c-axis perpendicular to the substrate surface.¹⁵⁴

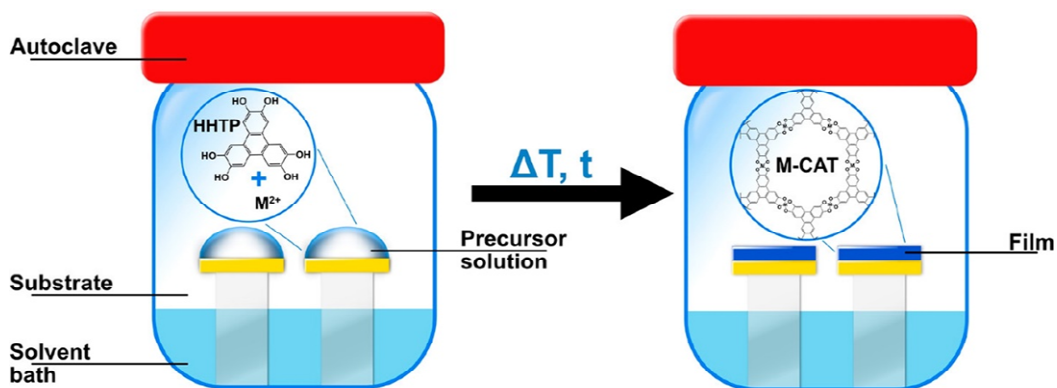


Figure 2.22: Schematic illustration of the vapour assisted conversion set-up used by Mahringer *et al.* Precursor metal salt and ligand solutions are placed on the desired substrates which are situated on elevated platforms above the solvent bath. After heating in an autoclave, thin films of the MOF grow on the substrate. Reproduced from reference 154.

Liquid-phase epitaxy has also been used to synthesise HXTP MOFs directly on substrates. Of particular note is the 2020 work by Wu *et al.* in which $\text{Ni}_3(\text{HHTP})_2$ was synthesised on single layer graphene in order to make transparent functional films. The single layer graphene template was submerged in the saturated ligand and metal salt solution to trigger MOF growth on the graphene surface.¹⁵⁵ Success has also been reported in synthesising $\text{Cu}_3(\text{HITP})_2$ MOF around polystyrene nanosphere templates. Miao *et al.* report coating nanospheres with HATP ligand and drop-casting them onto the desired substrate. An alkaline copper salt solution was then dropped on top allowing the MOF to form in the spaces between the nanospheres. THF was used to dissolve the nanospheres to leave an inverse opal MOF structure with hierarchical porosity.¹⁵⁶

In 2021 Kim *et al.* published a method to produce $\text{Cu}_3(\text{HHTP})_2$ MOF films with embedded Pt nanoparticles via solution shearing.¹⁵⁷ They mixed MOF and Pt nanoparticle precursor solutions in the presence of NaBH_4 and flowed them through microfluidic channels on a shearing blade. The blade was then drawn across a heated substrate at an angle of 30° . The

solution flowed out of the microfluidic channels onto the substrate on which the MOF thin film grew with the Pt nanoparticles already embedded in the MOF.¹⁵⁷

Further progress in synthesising conductive MOFs in situ on insulating substrates was made by the Mirica and Wang groups at the end of 2022. Both groups published work describing how $\text{Cu}_3(\text{HHTP})_2$ could be synthesised directly on fibres through coating the fibres in copper nanoparticles and then exposing them to solutions of HHTP.^{158,159} Wang et al. use a multi-step method whereby the nanoparticles are first converted to $\text{Cu}(\text{OH})_2$ nanowires using a concentrated sodium hydroxide and ammonium persulphate solution for 20 minutes, before being submerged in a DMF/ H_2O HHTP solution for 2 hours at 80 °C. The work published by the Mirica group on the other hand describes how zero-valent copper nanoparticles deposited on a variety of woven substrates can be converted into conductive $\text{Cu}_3(\text{HHTP})_2$ MOF and then used as an effective gas sensor for NO and H_2S gases.¹⁵⁹ This paper highlights the benefits of the synthesis method in terms of its ability to be applied to a number of different substrates and how easy it is to control the location of MOF growth and so generate MOF in desired patterns. They did not report using similar methods to produce conductive MOFs based on Ni or on HHTP ligands. The authors utilise a neutral synthesis solution and describe how H_2O_2 gas must be bubbled through the solution in order to reduce the synthesis time from 12 hours to 15 minutes.

Electrochemical growth of HXTP MOFs is a promising synthesis route in terms of substrate adhesion, MOF homogeneity and morphological control. Bradshaw et al. report how $\text{Cu}_3(\text{HHTP})_2$ can be synthesised on Cu anodes.¹⁶⁰ A positive potential is applied to the anodes to oxidise the Cu whilst submerging the electrodes in a solution of the linker, allowing the MOF to form adhered to the bulk Cu anode. For use in applications such as chemiresistive sensing, the MOF must be adhered to an insulating substrate. Therefore, polymethylmethacrylate (PMMA) in chlorobenzene was applied to the MOF film and cured

overnight before the MOF@PMMA could be peeled off from the copper anode.¹⁶⁰ This process is summarised in Figure 2.23.¹⁶⁰ Attempts to remove the PMMA from the MOF were not reported in this publication, but were subsequently described by Liu and co-workers who transferred the MOF@PMMA to a flexible polyethylene naphthalate substrate, which was then heated in acetone to dissolve the PMMA.¹⁶¹

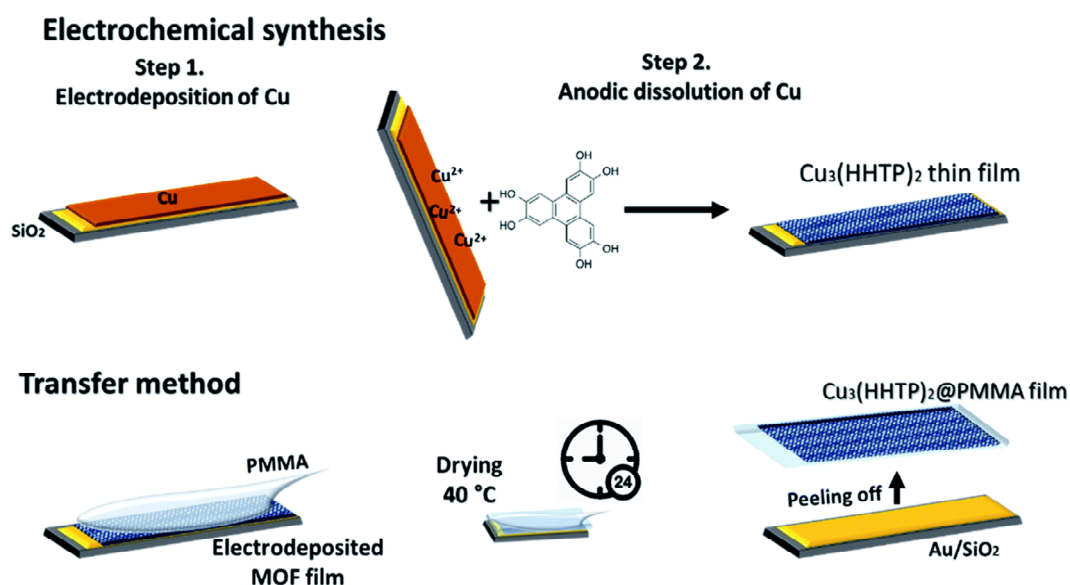


Figure 2.23: Schematic showing the steps involved in the electrochemical synthesis of Cu₃(HHTP)₂ on Cu anodes, and the subsequent film transfer. Cu is first electrodeposited on a Au/SiO₂ substrate. An applied potential triggers the anodic dissolution of Cu which results in MOF formation due to reaction with HHTP molecules in solution. For most electrical device applications, the conductive MOF must be adhered to an insulating substrate, PMMA is therefore applied to the film so that the MOF can be peeled off the conductive Au substrate. Reproduced from reference 160.

Li et al. reported a route to synthesise the same Cu₃(HHTP)₂ MOF electrochemically but on the cathode instead of the anode.¹⁶² For this method, bulk copper metal was not used, instead the copper source was provided by dissolved copper nitrate salt in solution with the ligand. A negative potential was applied to an FTO electrode, and O₂ gas was bubbled through the solution. The authors concluded that O₂ was reduced in the vicinity of the FTO cathode which then triggered reaction of the MOF precursors to form the Cu₃(HHTP)₂ adhered to the FTO.¹⁶²

2.4.3 Chemiresistive sensing of HXTP MOFs

Conductive MOFs in the HXTP family have been found to operate as effective chemiresistive sensors for a number of analyte gases. A small voltage can be applied across the MOF and the current flowing through it is measured. On adsorption of particular analytes, the current changes, allowing the MOF to operate as a chemiresistive sensor. This was first reported by Chen et al. who fabricated a chemiresistive formaldehyde sensor based on the 3D Co-based MOF, ZIF-67.⁸ The current flowing across the sensor at a constant applied voltage was measured as the sensor was exposed to varying concentrations of formaldehyde gas. A resistance against time plot was then produced, Figure 2.24 – left. From this, the response for each exposure is calculated as the change in resistance divided by the pre-exposure resistance. Plotting these values against the analyte concentration gives the plot in Figure 2.24 – right. For this sensor, we observe that the response-concentration is not linear at concentrations above 50 ppm, but is linear below 50 ppm, as depicted in the inset image. It is linear response vs concentration plots like these that enable limits of detection to be calculated, section 3.3.2.

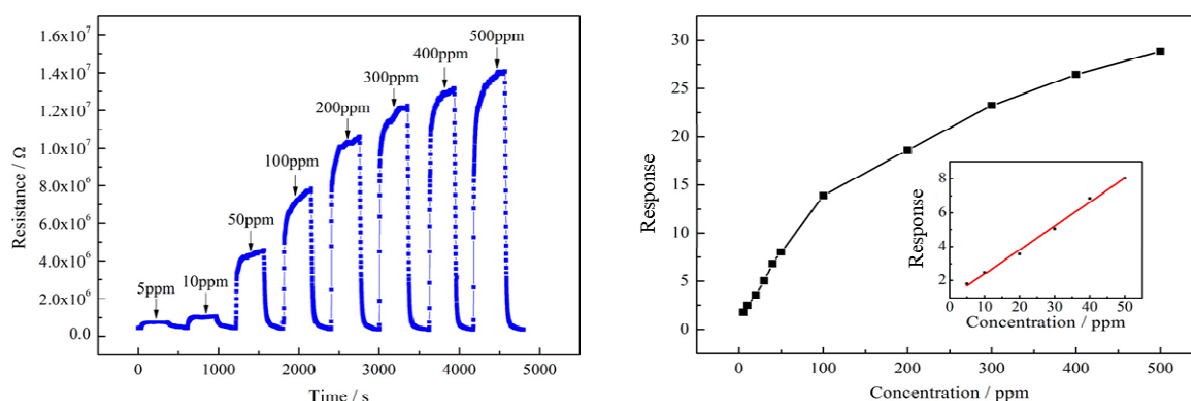


Figure 2.24: *Left* – Resistance vs time plot for a ZIF-67 MOF sensor exposed to formaldehyde gas with concentrations between 5 and 500 ppm. *Right* – Response for each exposure is calculated as the change in resistance divided by the initial resistance, this is plotted against analyte concentration. *Inset* – Response and concentration are linearly related at concentrations below 50 ppm. Reproduced from reference 8.

The first instance of HXTP MOFs operating as chemiresistive sensors was reported by Campbell et al. in 2015. They fabricated $\text{Cu}_3(\text{HITP})_2$ and $\text{Ni}_3(\text{HITP})_2$ sensors by drop casting the MOFs onto Au electrodes. They found the $\text{Cu}_3(\text{HITP})_2$ sensor to respond to NH_3 gas of concentrations down to 0.5 ppm, whilst the analogous $\text{Ni}_3(\text{HITP})_2$ sensor gave no measurable resistance response at any concentration.¹⁶³ The same research group then fabricated $\text{Cu}_3(\text{HHTP})_2$, $\text{Cu}_3(\text{HITP})_2$ and $\text{Ni}_3(\text{HITP})_2$ sensors and combined them into a single sensing array. They exposed the sensing array to a number of different organic analytes at 200 ppm and recorded the conductivity changes to produce the plot shown in Figure 2.25.¹⁵² Analysis of the sensing responses with principal component analysis produced the plot in Figure 2.26 in which distinct groups corresponding to different analyte functionalities are visible.¹⁵²

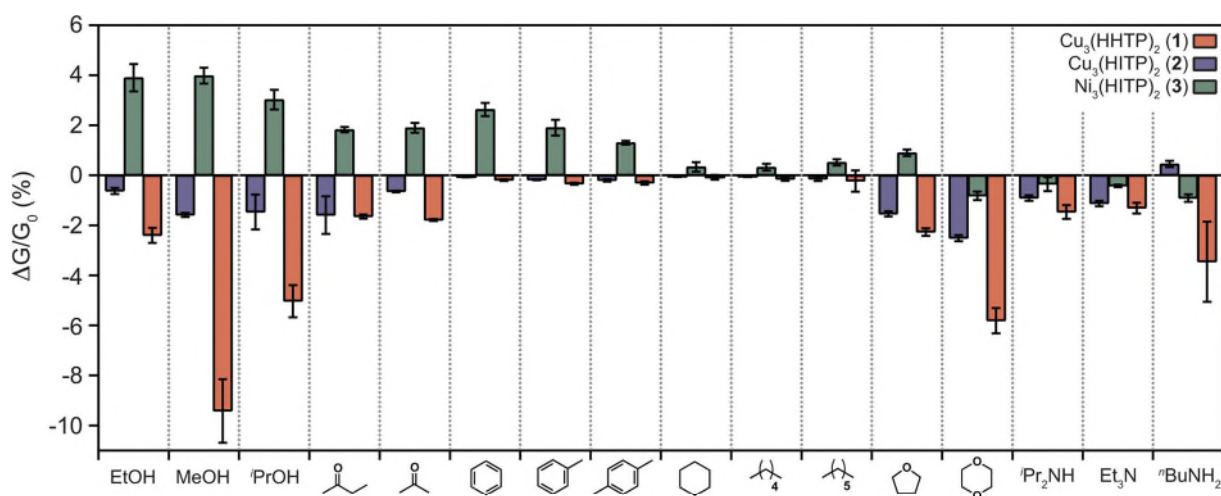


Figure 2.25: Changes in conductance observed when $\text{Cu}_3(\text{HHTP})_2$, $\text{Cu}_3(\text{HITP})_2$ and $\text{Ni}_3(\text{HITP})_2$ MOFs were exposed to 200 ppm of various organic analyte gases. Each MOF represents a different component of the chemiresistive sensor array fabricated by Campbell et al. The same analyte gas can cause opposite resistance changes depending on the MOF used. Reproduced from reference 152.

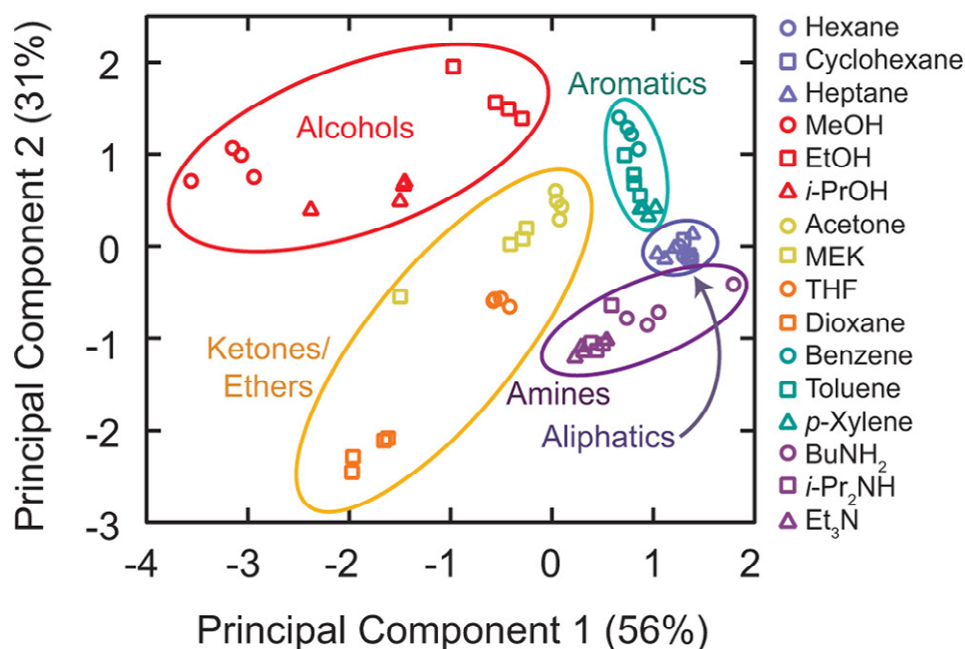


Figure 2.26: Principal component analysis for the responses of the 3-component MOF array fabricated by Campbell et al. Groups for different types of analytes can be identified; alcohol, aromatics, amines, aliphatics and ketones/ethers. Reproduced from reference 152.

Further potential for fabricating selective chemiresistive sensors was discovered by Yao et al. when they found that thin-films of Cu₃(HHTP)₂ fabricated by spray layer-by-layer epitaxy gave a 129 % resistance increase on exposure to 100 ppm of NH₃ gas, whilst exposure to 10 other gases including benzene, carbon monoxide and methanol gave only small resistance changes.¹⁴⁸

A lot of work on HXTP gas sensing has been done by the Mirica group. Their first work in this area involved drawing electrodes onto polymer films with a graphite pencil, shrinking the electrodes down by heating the film, then submerging the graphite-decorated film in a solution of the MOF precursors. With this method rod-like Cu₃(HHTP)₂ and Ni₃(HHTP)₂ particles formed on the polymer substrates with the electrodes on. The chemiresistive responses of the two different MOF sensors were considered together in a two component array, which enabled NH₃, NO and H₂S gases to be distinguished at concentrations between 10 and 80 ppm.¹⁶⁴ They then synthesised Ni₃(HHTP)₂ and Ni₃(HITP)₂ MOFs directly on textile substrates by

submerging the clean textiles in the hydrothermal synthesis solution. Both sensors responded to NO and H₂S gases, with the Ni₃(HITP)₂ sensor responding to give calculated limits of detection of 0.16 ppm for NO and 0.52 ppm for H₂S.¹⁶⁵ The same research group also report ball-milling HHTP-based MOFs with graphite, then abrading the mixture onto inter-digitated electrodes on paper substrates. The resulting Fe, Cu, Co and Ni – HHTP sensors were then combined into an array with which NH₃, NO, H₂S and H₂O gases could be distinguished from one another.¹⁵³

2.5 Sensing mechanisms

Whilst the sensing responses of HXTP MOFs to a number of analyte gases have been reported, relatively little has been said about the sensing mechanisms responsible for their performance. The interaction of Cu and Ni HHTP and HITP frameworks with NH₃ gas is the most studied of the chemiresistive sensing mechanisms.

In the pioneering sensing studies performed by Campbell et al. Cu₃(HITP)₂ MOF was found to respond with a reversible resistance increase on exposure to NH₃, whilst Ni₃(HITP)₂ was found to not respond. The authors rationalised this in terms of the different d-electron counts of the Cu²⁺ and Ni²⁺ ions which leads to the Cu MOF having a higher fermi level.¹⁶³ The mechanism of interaction of the isostructural Cu₃(HHTP)₂ MOF with NH₃ was studied experimentally and computationally by Rubio-Giménez et al. They used IR, PXRD and dispersion corrected DFT to confirm that the Cu centre was the site of interaction with the NH₃ analyte.¹⁴⁴ Their DFT calculations suggested that increasing the interlayer separation in the MOF increased the band gap, indicating that the through-space π - π charge transport route plays a significant role in the electronic structure of the MOF. Further calculations found that

incorporation of NH_3 guests disrupted the square planar geometry of the Cu^{2+} centre to a distorted trigonal prism, accompanied by an increase in interlayer separation of approximately 3 %. This finding was corroborated by PXRD experiments that found a reversible increase in interlayer separation on exposure to NH_3 , and infrared reflection absorption spectroscopy, IRRAS, that showed a peak at 1620 cm^{-1} corresponding to $\text{Cu}^{2+}\text{---NH}_3$ coordination.¹⁴⁴ The authors believe that changes in conductivity on NH_3 exposure are likely due to increases in interlayer separation reducing the through-space charge transport efficiency and so increasing the band gap. It should be noted however, that the calculations were performed in an environment where one NH_3 molecule is present per metal ion. For the case of high sensitivity gas sensing experiments, where MOF samples are exposed to 5 ppm of NH_3 for 60 s for example, we consider it more likely that NH_3 donating electrons to the metal centre and so reducing the hole concentration is the dominant mechanism responsible for the measured resistance increase.

The sensing responses of Cu and Ni, HHTP and HITP MOFs to NH_3 gas were later studied by Stolz et al.¹⁴³ FTIR performed in situ as the MOFs were exposed to NH_3 gases found evidence for NH_3 interacting with the MOFs in two different ways, implying that the Cu MOFs contain both Brønsted and Lewis acidic sites. They concluded that the MOFs act as Lewis acids when the NH_3 molecules donate electrons to the metal sites directly, and as Brønsted acids when the NH_3 molecules accept protons from H_2O molecules coordinated to the vacant sites on the metal, as illustrated in Figure 2.27. When the MOF acts as a Brønsted acid, peaks corresponding to NH_4^+ ions are present in the FTIR spectrum, whilst peaks corresponding to new Cu-N interactions appear when the MOF acts as a Lewis acid. Analysis of the FTIR data lead Stolz et al. to the conclusion that the Lewis acid response dominated for the $\text{Cu}_3(\text{HITP})_2$ MOF, whilst a combination of Lewis acid and Brønsted acid behaviour was responsible for the interaction of $\text{Cu}_3(\text{HHTP})_2$ with NH_3 . Whilst this evidence suggests that

slightly different interaction mechanisms are taking place for the two MOFs, both involve NH_3 interacting with the MOFs at the metal centre above and below the conjugation plane, which would lead to slight increases of the interlayer separations, and therefore, by Rubio-Giménez et al.'s conclusion, increased band gap and resistance. Equally, NH_3 donating electrons to the Cu^{2+} metal centre thus reducing the hole concentration, would result in a decrease in current flow via the conventional p-type semiconductor sensing mechanism.

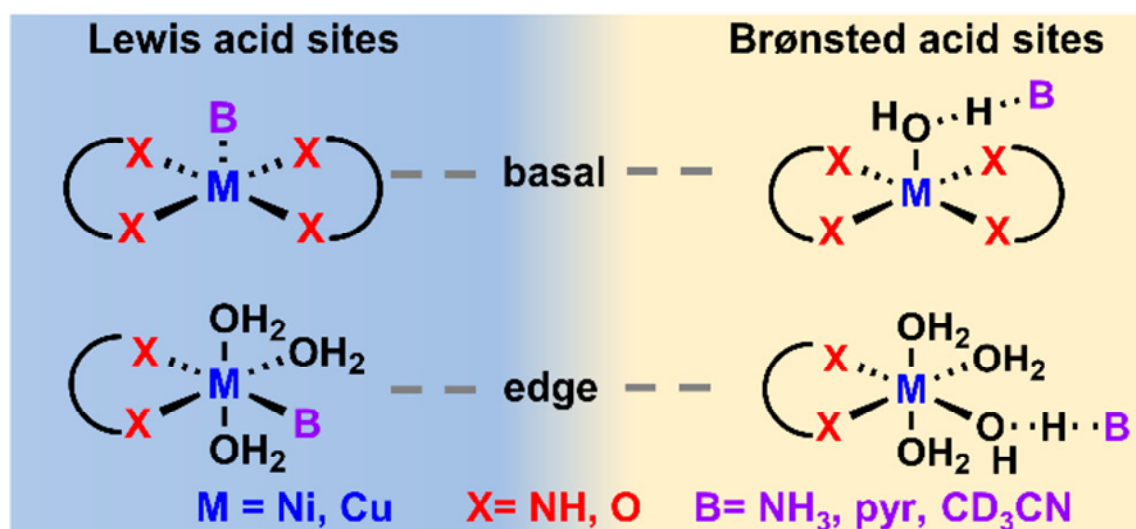


Figure 2.27: The host-guest interactions proposed for Cu and Ni HHTP and HITP MOFs. Reducing analyte gases, B, can interact directly with the metal centres, at Lewis acid sites, or with H_2O molecules bonded to the metal centres, Brønsted acid sites. Reproduced from reference 143.

Further work by Stolz et al. used XPS and EPR techniques to look at charge transfer between the ligand and metal centres when all 4 MOFs were exposed to basic gases.¹⁴³ These experiments showed a shift in redox balance between the ligand and metal for the Cu-based MOFs on interaction with NH_3 , but no such change for either of the Ni-based MOFs. This is likely due to the more flexible valency of Cu compounds, with both Cu^+ and Cu^{2+} being stable, whilst Ni^{2+} is by far the most stable Ni ion. In the case of $\text{Cu}_3(\text{HHTP})_2$ interacting with NH_3 , XPS found the ligand to store more of the charge than the metal compared to the MOF pre-exposure. On the other hand, when the $\text{Cu}_3(\text{HITP})_2$ MOF interacted with NH_3 , XPS found the

ligand to be oxidised and the metal reduced relative to the pristine MOF. The absence of similar evidence for the communication between the ligand and metal centre to maintain charge neutrality and enable the interaction with NH_3 for the Ni MOFs can rationalise why no change in conductivity is observed when $\text{Ni}_3(\text{HHTP})_2$ or $\text{Ni}_3(\text{HITP})_2$ MOFs are exposed to NH_3 gas.

The sensing mechanism responsible for any conductivity changes when HXTP MOFs interact with NO_2 is rarely addressed in publications. Koo et al. found $\text{Cu}_3(\text{HHTP})_2$ MOFs with embedded Pt or Pd nanoparticles to respond with resistance decreases on exposure to NO_2 gas. The authors attributed this to the NO_2 withdrawing electrons from the framework by interacting with the metal site, causing the resistance of the p-type semiconducting frameworks to increase.¹⁶⁶ Jo et al. investigated the visible-light activated sensing response of $\text{Cu}_3(\text{HHTP})_2/\text{Fe}_2\text{O}_3$ hybrids to NO_2 gas and concluded that Lewis acid-base interactions between the Cu centres and the NO_2 gas were responsible for the resistance decreases observed. They postulate that as the $\text{Cu}_3(\text{HHTP})_2$ MOF contains both Cu^+ and Cu^{2+} centres, the NO_2 could interact with the Cu^+ centres forming N-nitro, O-nitrito or O,O' bidentate complexes.¹⁶⁷ Whichever complex formed, this would result in NO_2 withdrawing electrons from the framework and increasing the hole concentration, therefore decreasing the resistance. Experiments reported in this thesis however, suggest that the ligand is the more likely site for interaction with NO_2 . This will be discussed in more detail in chapter 4.

2.6 Conclusion

The high porosities and tuneable functionalities of MOFs make them attractive candidates for use in a variety of applications. They are also highly promising materials for use in

chemiresistive sensing media. Conductive MOFs can be synthesised in a number of ways but to aid their integration into electronic devices such as chemiresistive sensors, there is a demand for reliable ways of generating uniform distributions of the MOFs in situ on the desired substrates. The sensing mechanisms responsible for the resistance changes of HXTP-based MOFs on exposure to reducing and oxidising gases such as NH_3 and NO_2 are not yet fully understood.

Chapter 3

Experimental techniques

The general experimental techniques used to undertake the work described in chapters 4 to 7 of this thesis are discussed in this chapter. Since chapters 5 and 6 focus on the development of novel methods of MOF synthesis, the specifics of these methods will not be discussed in this chapter. However, the general nanoparticle deposition and chronoamperometry techniques that are used are described in sections 3.1.3, and 3.1.4. In sections 3.1.1 and 3.1.2, conventional solution synthesis methods for generating the desired MOFs are described as well as the typical methods of fabricating sensors from these by depositing them on electrodes. In section 3.2 the analytical techniques used to confirm the presence of the desired MOFs are detailed, whilst in section 3.3, the equipment and techniques used to assess the performance of the sensors are explained.

3.1 Sensor fabrication

A number of different methods are used in this work to produce MOFs and sensors from these MOFs. These include solution synthesis from metal salts, synthesis from metal nanoclusters, and electrochemical growth.

3.1.1 Solution synthesis of conductive MOFs

Four different electrically conductive MOFs were synthesised via solution synthesis methods. These MOFs are all formed of similar 2D hexagonal layered sheets, as depicted in Figure 3.1. The MOFs are based on Cu or Ni centres linked by hexa-substituted triphenylene organic

linkers with amine or oxygen functional groups. The solution synthesis methods used to synthesise $\text{Cu}_3(\text{HHTP})_2$, $\text{Cu}_3(\text{HITP})_2$, $\text{Ni}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HITP})_2$ MOFs will be described in the remainder of this section.

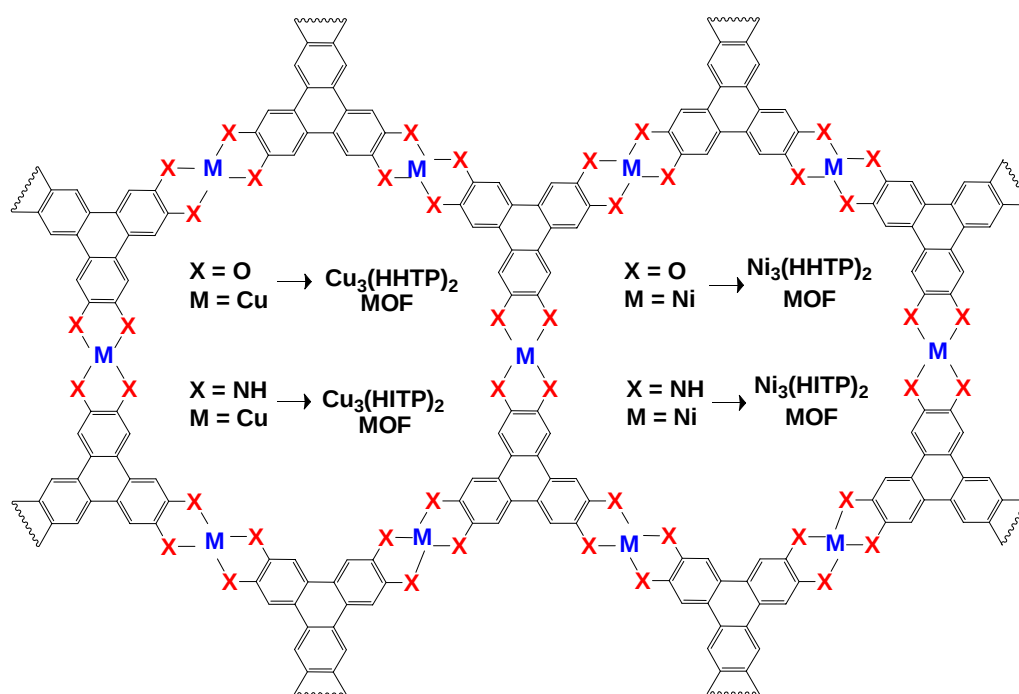


Figure 3.1: Structure of a single 2D layer of the four hexa-substituted triphenylene-based MOFs synthesised via solution synthesis during this project. These sheets stack to form 3D MOF crystals. *M* represents the metal centres (Cu or Ni), whilst *X* = NH for HITP MOFs, and *X* = O for HHTP MOFs.

As discussed in section 2.2, conductive MOFs made from hexahydroxytriphenylene, HHTP, ligands were first synthesised from solution.¹⁴¹ Adaptations of this first synthesis published by Yaghi et al. in 2012 were used to synthesise $\text{Cu}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HHTP})_2$ MOFs for the work contained in this thesis. The methods involve reaction of a soluble metal salt with the HHTP ligand in a 3:2 ratio. Copper trifluoroacetate and nickel acetate tetrahydrate were the salts used here, both of which were purchased from Sigma-Aldrich, USA. The HHTP ligand was purchased from both TCI Chemicals, Japan and Fluorochem, UK. The syntheses were

performed in 28 mL vented vials in an aqueous solution. The ligand was always present in excess. The vials were heated to 85 °C for between 24 and 48 hours depending on the MOF to be synthesised. Gravity filtration and washing with deionised water and acetone yielded the MOFs as microcrystalline blue/black powders.

Inspired by the work of Hoppe et al., $\text{Cu}_3(\text{HHTP})_2$ MOF was also synthesised from a copper (II) nitrate trihydrate salt, with the addition of between 0 and 50 equivalents of ammonia solution.¹⁶⁸ This resulted in the formation of flatter MOF crystals. The effect of morphology on sensing ability could then be investigated.

The analogous MOFs based on 2,3,6,7,10,11-hexaiminotriphenylene ligands, $\text{Ni}_3(\text{HITP})_2$ and $\text{Cu}_3(\text{HITP})_2$, were also synthesised via solution synthesis methods. The organic linker was purchased in its hydrogen chloride coordinated form ($\text{HATP} \cdot 6\text{HCl}$) from BLD Pharmatech, Germany. The $\text{Cu}_3(\text{HITP})_2$ synthesis was carried out according to the method published by Campbell et al.¹⁶³ Copper sulphate pentahydrate (7 mg, 0.028 mmol) was dissolved in deionised water (2 mL) and ammonia solution (75 μL , 19.4 M) was added. In a separate vial, the HATP starting material (10 mg, 0.019 mmol) was dissolved in deionised water (3 mL). The two solutions were then combined and left to stand at room temperature for 3 hours. Gravity filtration and washing with deionised water and acetone yielded the MOF as a microcrystalline black powder. Both the ammonia solution and copper sulphate pentahydrate salt were purchased from Sigma-Aldrich, USA. Synthesis of the $\text{Ni}_3(\text{HITP})_2$ MOF involved dissolving the $\text{HATP} \cdot 6\text{HCl}$ (7 mg, 0.019 mmol) and nickel acetate tetrahydrate salt (10 mg, 0.040 mmol) in deionised water (4 mL). The mixture was heated to 85 °C in a vented 28 mL vial for 12 hours. After cooling, gravity filtration and washing with deionised water and acetone was performed to yield the MOF as a microcrystalline black powder.

3.1.2 Interdigitated electrodes and drop casting

To be used as a chemiresistive sensor, conducting MOF must bridge an insulating gap between two conductors. Interdigitated electrodes, IDEs, consist of two main electrodes with conductive fingers that resemble interlocking combs. The two electrodes are arranged with their fingers extending towards each other so that the fingers of one electrode can occupy gaps between the fingers of the other electrode. The result is an IDE that is insulating to current flowing from one contact pad to the other, but only a small distance between the metallic fingers must be occupied by conductive material for current to flow, Figure 3.2 (a).

Since Achmann et al. first deposited conductive MOF onto IDEs for sensing in 2009, they have become widely used as substrates to deposit chemiresistive MOFs onto.¹⁰⁸ Such IDEs are now widely available for purchase, often costing under £10 per unit. IDEs using gold, platinum and copper electrodes on glass, plastic and ceramic substrates are all available.

The IDEs used for most of the experiments reported in this thesis were purchased from Micrux Technologies (Spain). The metal used was Pt and the substrate was glass. The insulating gaps between the electrode fingers were 5 μm wide. Most of the work where IDEs were required could be carried out using the standard IDEs depicted in Figure 3.2 (b). The electrochemical synthesis described in chapter 6 was carried out on the custom electrodes depicted in Figure 3.2 (c). The IDEs in (b) and (c) differ only in the distance between the contact pads and the interdigitated region. Using longer electrodes for the electrochemical synthesis avoids contamination of the electrode holder with the synthesis solution.

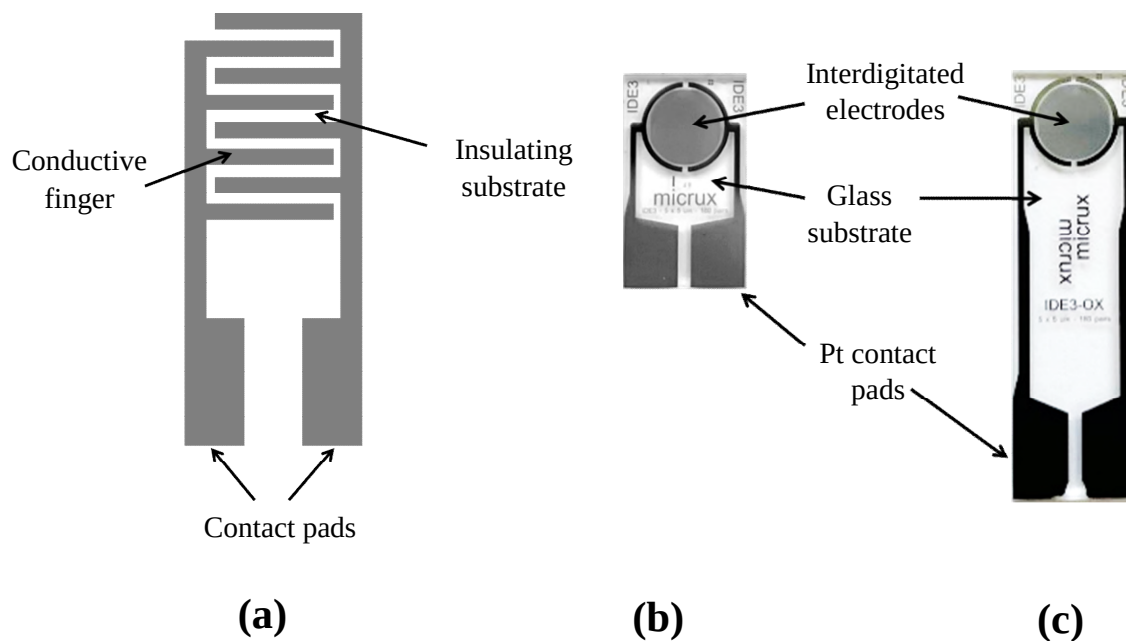


Figure 3.2: (a) Schematic representation of a typical interdigitated electrode, IDE, comprised of fingers of conductive material (grey) separated by gaps where the insulating substrate is exposed (white). (b) Photograph of the standard Micrux Technologies IDE. (c) Photograph of the custom made longer length IDEs from Micrux Technologies. Conductive material is deposited to bridge the insulating gaps and allow current to flow when a voltage is applied between the contact pads.

For instances where the MOF is not synthesised in situ on the IDEs, it is typically suspended in a solution and drop-cast onto the electrodes. This can lead to non-uniform distribution of the MOF on the electrode, which can make it hard to repeatedly fabricate sensors with the same resistances. This in turn can make it difficult to optimise the amount of MOF for best sensor performance. To minimise uneven drying of the MOF suspension droplet, different solvent combinations were used. The solvents used included ethanol, DI water, 1,3-propane diol, isopropyl alcohol and acetone.

3.1.3 Metal nanocluster deposition

Instead of using metal salts as the metal source for MOF formation, the work described in chapters 6 and 7 uses metal nanoclusters. These were deposited on a variety of substrates on

which the MOFs were then synthesised. The process of nanocluster generation and deposition will be discussed here.

A room temperature magnetron sputtering source, the NL50 from Nikalyte Ltd., was used to deposit nanoclusters of copper and nickel onto various substrates. Magnetron sputtering involves the use of magnets to form ‘electron traps’ so that high discharge currents can be accessed even at low temperatures and voltages.¹⁶⁹ A target of the metal to be deposited is selected and inserted into the set-up, Figure 3.3,¹⁷⁰ where it acts as a cathode. The resulting electric field acts to accelerate the ions of the Ar buffer gas towards the target where they sputter atoms of the target metal and trigger the emission of secondary electrons. By positioning magnets as illustrated in Figure 3.3, the magnetic field traps electrons in the highlighted region, increasing the plasma charge density and ionising more of the Ar atoms in the vicinity which increases the sputtering rate over this part of the target. The result is a higher sputtering rate than an analogous system without magnets, and the formation of circular rings (erosion rills) on the target where it has been eroded more heavily, Figure 3.3 - right.¹⁷⁰ The produced clusters pass through a quadrupole mass filter, QMF, and then flow to the substrate due to a pressure gradient inside the machine.

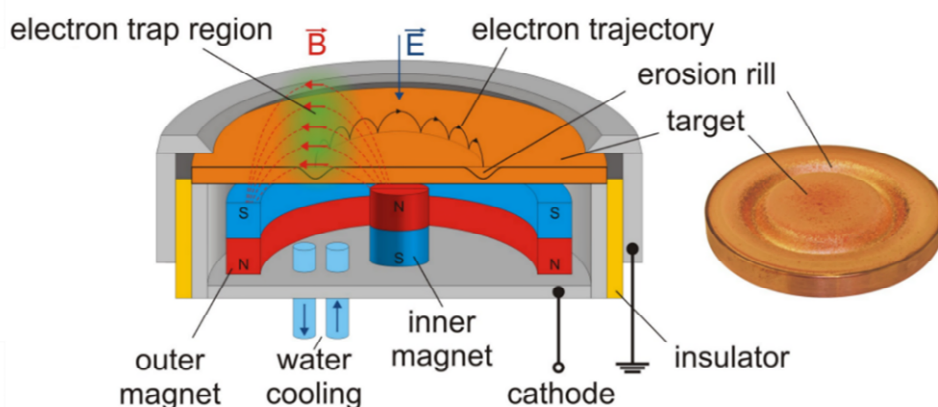


Figure 3.3: **Left** – Magnet, electrode and target configuration in a magnetron sputtering set-up like the Nikalyte NL50. The combination of magnetic and electric fields creates an electron trap region which increases the target sputtering rate. **Right** – Metallic target with erosion rill due to increased sputtering in the electron trap region. Reproduced from reference 170.

With the NL50 device, nanoclusters can be deposited on any substrate that will fit on the deposition plate (approximately 10 cm in diameter). For the work in this thesis, copper and nickel nanoclusters were deposited on glass IDEs (Micrux Technologies, Spain - Figure 3.2), white card (WHSmith, UK), 200 thread count cotton percale (Dalston Mill Fabrics, UK) and Au (111) on mica (George Albert PVD, Germany).

Using this apparatus, it has been reported that the size of the clusters varies with the age of the target, in that newer targets produce clusters formed of fewer atoms than targets that have been eroded for cluster deposition previously.¹⁷¹ For the case of copper nanoclusters deposited on silicon, the clusters were reported to diffuse and merge to form larger islands over time.¹⁷¹ When copper nanoclusters were deposited on the glass IDEs for this project, they were annealed at 200 °C for 2 hours in air before electrochemical MOF synthesis (chapter 7). The aim of this was to improve adhesion of the nanoclusters to the IDE and improve conductivity by initiating necking between the particles. It is suspected that these necking and merging effects dominate over dewetting of the nanoclusters from the substrate at 200 °C, which is consistent with the measured decrease in resistance after annealing. Decreases in measured resistances were consistently observed when comparing the same nanocluster-decorated IDE sample before and after annealing. For example, for an IDE with 5 µm insulating gaps (Micrux Technologies, Spain), with 1000 ng cm⁻² of copper nanoclusters deposited on it, the pre-annealing resistance was 0.792 MΩ, whilst the resistance after annealing was 112.0 kΩ.

As a paid for service, I was not able to control the age of the target used, so there will be slight variations in cluster size for each run as a result. The argon flow rate and magnetron current also effect the size of nanoclusters deposited, as well as the deposition rate. Reports indicate that increasing the argon flow rate from zero increases the size of nanoparticles deposited due to increased sputtering making more material available to form nanoparticles, before reaching

an optimum flow rate above which the deposition rate and particle size decreases. This decrease is due to particle growth suppression as a result of the increased frequency of inelastic collisions between the nanoparticles and buffer gas.¹⁷² Increasing the magnetron current increases the particle size and deposition rate by increasing the rate and amount of metal particles present in the gaseous state at any given time.¹⁷² The QMF typically permits particles between 2 and 15 nm through, but TEM analysis reveals particles with diameters above this range. This effect is attributed to the inevitable aggregation of the clusters on the surface. The size of the particles obtained can therefore only accurately be determined by analysis after deposition.¹⁷³

Both the argon flow rate and magnetron current can be easily changed on the NL50 machine. On consultation with members of the Nikalyte team, parameters for both the current and flow rates were set. For deposition of copper, an Ar flow rate of 35 sccm was used and a magnetron current (power) of 330 mA. These conditions typically gave a discharge voltage of around 650 V, significantly lower than the voltages required in magnetron-free sputtering systems.¹⁶⁹ The same current was used for the nickel deposition, but a slightly smaller Ar flow rate of 20 sccm was used.

The settings were altered after commencing the deposition if the deposition rate started dropping. A variety of different deposition depths between 5000 and 8000 ng cm⁻² were used, with typical deposition rates between 2 and 50 ng cm⁻² s⁻¹. If the same amount was deposited as a dense continuous film instead of as discrete nanoclusters, this would equate to film thicknesses between 5.5 and 8.9 nm.

3.1.4 Chronoamperometry

Electrochemical MOF synthesis was carried out using chronoamperometry, CA. A standard 3-electrode set-up was used, Figure 3.4. In this work, the metal source for the MOF was present on the working electrode either as nanoclusters or bulk metal such as copper tape or foil. The bulk metal was used instead of metal salt in the solution. These working electrodes were then submerged in a solution of ligand and electrolyte. The potentiostat applied a constant potential between the working and reference electrodes to oxidise the metal source and initiate reaction with the ligand in solution. The potential is set between the working and reference electrodes whilst the majority of the current flows between the working and counter electrodes. An electrolyte is added to the solution where it dissociates into electrochemically stable complex ions that enable current transport through the solution, preventing charge build up in the vicinity of the electrodes.

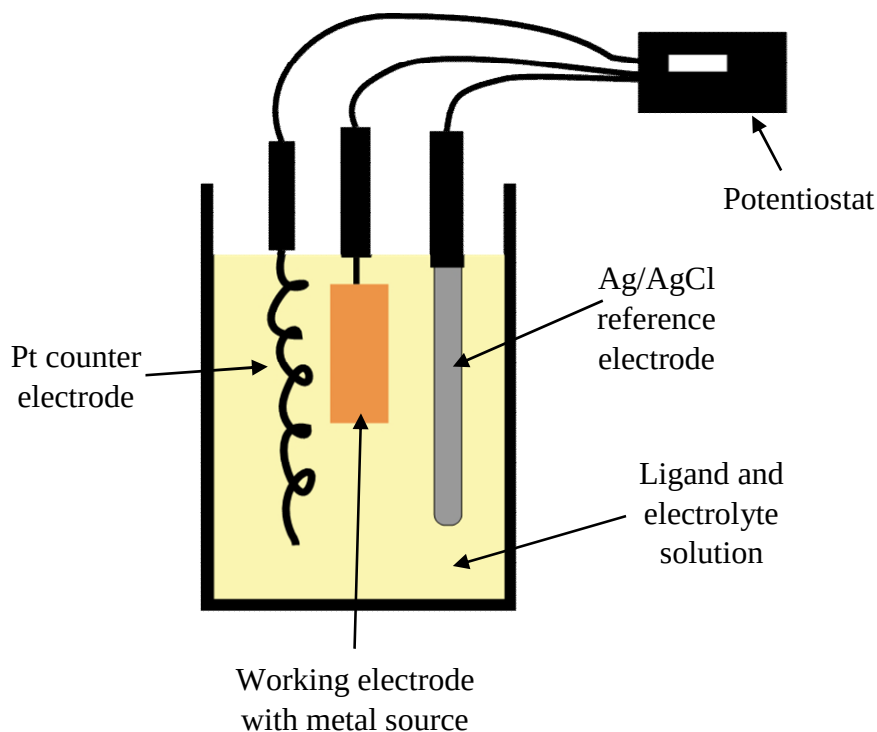


Figure 3.4: Schematic of the 3-electrode cell used for electrochemical synthesis. The working electrode is decorated with the metal that will act as the metal node in the resulting MOF. The potentiostat applies a potential difference between the working and reference electrodes. Most of the current flows between the counter and working electrodes to reduce consumption of the reference.

For the experiments performed in Chapter 6, a 2.6 mM solution of 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and 0.021 M solution of methyl tetrabutyl ammonium sulphate (TBMAMS) electrolyte was made up in a 4:1 ethanol and deionised water mixture. An Ag/AgCl reference electrode (IJ Cambria Scientific Ltd., UK) was used in addition to a Pt coil counter electrode (BASi MW-1033 Coiled Pt Counter Electrode, Alvatek Ltd., UK). The working electrodes were either copper foil, copper tape or long Pt IDEs (section 3.1.2) decorated with copper nanoclusters. The potential was applied using a PGASTAT204 Autolab potentiostat (Eco Chemie, Netherlands) controlled by a PC with NOVA 2.1 software.

3.1.5 Cyclic voltammetry

Cyclic voltammetry, CV, is a technique commonly used for analysing the oxidation and reduction capabilities of a species. The technique typically uses a 3-electrode electrochemical cell like that depicted in Figure 3.4. Instead of applying a constant potential between the reference and working electrodes as in CA, in CV the potential is ramped from a set value to a minimum or maximum before being reversed. The applied potential can be set to linearly increase and decrease multiple times in a given experiment, as depicted in Figure 3.5. The current flowing between the counter and working electrodes is recorded as the potential is changed, and peaks arise when redox events occur on the electrodes. The potential at which these peaks occur and how they change with increasing number of cycles can give us information about redox chemistry occurring in the system.

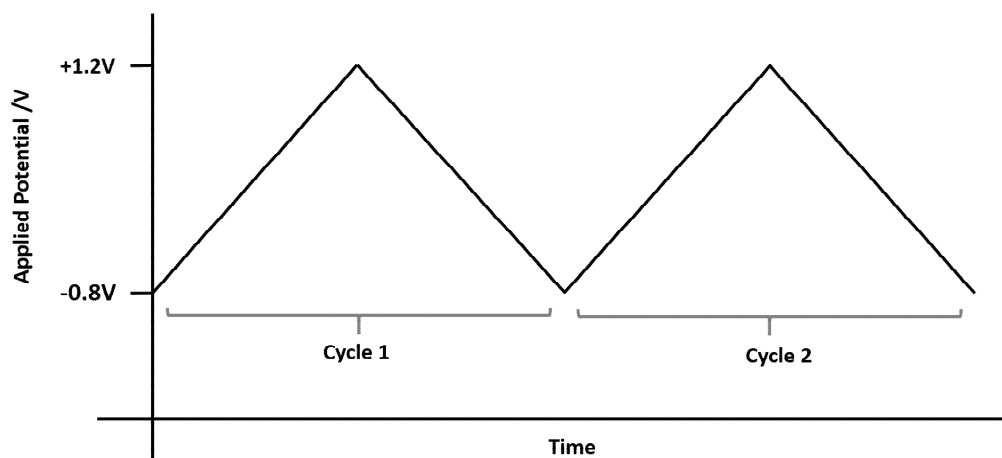


Figure 3.5: Example plot to illustrate the potential cycling used in cyclic voltammetry. The potential is linearly ramped between upper and lower limits as the current flow is measured. Peaks in the resulting potential vs current plot can give us an insight into the redox processes taking place.

To investigate the electrochemical growth of $\text{Cu}_3(\text{HHTP})_2$ from Cu nanoclusters as described in chapter 6, CV was performed. In this experiment the same 2.6 mM solution of HHTP and 0.021 M solution of the TBMAMS electrolyte in 4:1 ethanol/DI water solution was made up and used in the 3 electrode set-up depicted in Figure 3.4. The potential was ramped from -0.8 V to 1.2 V and then reversed for 40 cycles, at a rate of 0.02 V s^{-1} . The results of these experiments will be discussed in chapter 6.

3.2 Characterisation techniques

A number of characterisation techniques were used throughout this project. For the novel synthesis methods described in chapters 5 and 6 sample characterisation is of particular importance to prove that the new methods have been successful in making the desired MOF. Since the methods use nanoparticles coated on small areas of various substrates as the metal source for the MOF, the MOF is synthesised in small amounts, most of which is strongly adhered to the substrates. A distinction is therefore made between analytical techniques that

can be performed with the MOF still adhered to the substrate, and those for which bulk MOF powder must be obtained.

3.2.1 Electron microscopy

Scanning electron microscopy, SEM, involves detecting the secondary electrons emitted from a sample as a highly focused electron beam is rastered across the specimen.¹⁷⁴ It was the main imaging technique used in this project, and was valuable for determining sample morphology and comparing the morphologies of samples made using different synthesis conditions. A Merlin Analytical SEM machine was used (Zeiss, Germany), with most images taken with either the standard secondary electron detector or the in-lens detector. Operating voltages between 3 kV and 8 kV were used as a compromise between resolution and sample damage prevention. The probe current was 100 pA. Imaging of the MOFs could be carried out in situ on all of the substrates used, including fabric, paper and glass IDEs. Whilst the MOFs are conductive, they were largely deposited on insulating substrates. Care was taken to electrically connect the MOF to the SEM holder to prevent charge build up hindering imaging. For the glass IDEs, a holder with copper screws that could be rotated and connected to the contact pads of the IDEs were used. For the fabric and paper samples, conductive contacts were drawn on with silver dag which was then connected to the holder with conductive tape.

Energy-dispersive X-ray spectroscopy, EDX, was carried out on the same Zeiss Merlin electron microscope. In this technique, the incident electron beam knocks out electrons from the inner shells of an atom. Electrons occupying outer shells then move to fill the inner shell vacancy resulting in the release of an X-ray with energy equal to the energy difference between the levels, which is characteristic of a particular element.¹⁷⁵ The X-rays are detected by the EDX detector and can be used for elemental analysis. In this project EDX has been

used primarily to determine the elemental composition of features with different morphologies and to identify by-products and impurities in order to inform decisions about how the reactant ratios should be changed.

3.2.2 Powder X-ray diffraction

Powder X-ray diffraction, PXRD, experiments can be used to calculate the lattice parameters of polycrystalline samples such as the MOFs synthesised in this project. When a sample with long-range order is irradiated with electromagnetic radiation in the X-ray region, diffraction occurs as the atomic spacing is of the order of magnitude of the wavelength of the incident X-rays.¹⁷⁶ Incident X-ray beams are reflected off lattice planes in the crystal. When the incident beam hits the planes at certain angles, the path difference between beams reflected off different parallel planes will be such that they can interfere constructively, leading to a peak in intensity measured by the detector. The sample is rotated within the X-ray beam to produce a pattern of spots corresponding to orientations that give peaks in intensity of radiation reaching the detector.¹⁷⁷ For polycrystalline samples such as powders, the diffraction patterns from each crystal will overlap to produce a set of rings instead of a pattern of spots. These rings correspond to cones of diffracted X-rays as depicted in Figure 3.6.¹⁷⁸ The angle of the detector to the sample, or equivalently the semi-angle of the cone, at which the intensity peaks occur, can be used to generate a plot of diffracted intensity as a function of angle, 2θ . By looking at the ratio of 2θ values at which the peaks in intensity occur, the lattice type can be inferred, the peaks indexed and the lattice parameters calculated.

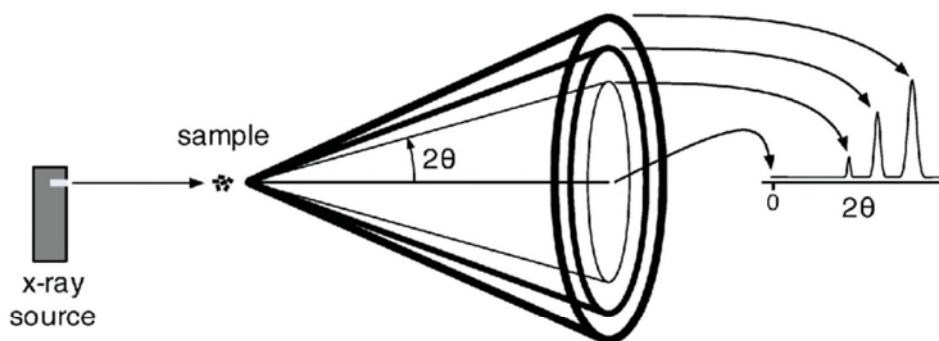


Figure 3.6: When illuminated with X-rays, powder samples produce cones of diffracted intensity with semi-angles, 2θ , governed by their crystal structure. The angles and intensities of the cones can be used to produce a PXRD plot. Reproduced from reference 178.

In this project, PXRD was used to confirm that the desired MOFs had been produced. By comparing the peak positions and therefore lattice parameters with those reported in literature, we were able to confirm that the new synthesis methods developed in this project were successful in generating the MOFs. The experiments were carried out on a Miniflex machine with a $1.54 \text{ \AA}$ CuK α X-ray source from Rigaku, Japan. Attempts to gather data from MOF in situ on the substrates were not successful, likely due to the high substrate surface roughness relative to the thickness of MOF layer. For the syntheses described in chapters 5 and 6, scraping the MOF off the substrates did not yield enough MOF for ex-situ experiments to be performed. The metal nanoparticles were therefore replaced by bulk metal foil or tape and the synthesis conditions replicated in order to obtain enough MOF to be able to do PXRD. The Java applet, ReciprOgraph (EPFL, Switzerland), was used to generate simulated PXRD data for known structures from their .cif files.

3.2.3 Transmission electron microscopy

Transmission electron microscopy, TEM, was used for the MOFs synthesised from nanoclusters when not enough material could be obtained for PXRD. Like SEM, TEM uses a

fine electron beam to probe the sample, but instead of collecting secondary electrons emitted from the sample or electrons reflected from the sample, TEM detects the electrons that are transmitted through it.¹⁷⁹ The resolutions obtained from TEM images are typically higher than those obtained with SEM, but there is a requirement for the particles to be thinner and more dispersed. For the MOFs described in this thesis, this means that they must be removed from the substrate on which they were synthesised and sonicated vigorously to break the particles apart. They can then be drop-cast onto a TEM grid from a dilute solution. If the samples are prepared optimally, TEM should be able to show the hexagonal in-layer structures of the MOFs, with the pore diameters visible. This would negate the need to obtain the a and b lattice parameters from techniques such as PXRD. In reality, it is very difficult to obtain thin enough particles for this to be seen. When such features are observed, the thinness of the sample in that region makes it difficult to capture an image before the sample is destroyed by the beam. Imaging the stacked layers side-on to the incident beam is however more straightforward. Such images depict lines corresponding to MOF sheets, separated by the interlayer separation, equivalent to lattice parameter c for the MOFs in this project.

In this thesis, TEM was used to determine the interlayer separation of MOF sheets when not enough material could be obtained for PXRD. The MOF samples were dispersed in ethanol and deposited onto Cu TEM grids with a lacey carbon film. The instrument used was a JEM-2100 machine manufactured by JEOL Ltd, Japan.

3.2.4 Raman spectroscopy

Raman spectroscopy was chosen over infrared spectroscopy as it was better able to probe the optical properties of the MOFs in situ on the IDEs on which they were synthesised. In this technique a laser is focused on an area of interest on the sample where it excites electrons to

a virtual electronic state. The electrons then fall back down to their original electronic state where they may end up in a different vibrational energy level and emit a photon. When electrons end up in a higher vibrational state than they started, the photon emitted will have lower energy than the incident laser beam, this leads to a peak in intensity at an energy below that of the incident laser.¹⁸⁰ These peaks are termed Stokes lines whilst peaks that occur at higher frequencies than the original laser are termed anti-Stokes lines. The peaks in the Raman spectra are therefore characteristic of the vibrational energy levels of the sample, which are dependent on the bond strengths and atomic masses of the sample components. In this project a confocal instrument with a 633 nm Ne-He laser and $\sim 2\ \mu\text{m}$ probe size was used (System 1000 instrument, Renishaw, UK) in which only the Stokes lines are recorded. Using this set-up Raman spectra between 500 and $3000\ \text{cm}^{-1}$ were recorded so that the spectra obtained for the starting materials and MOF products could be compared.

For some gaseous samples, rotational fine structure can be seen but for periodic solids such as the MOFs, distances between functional groups are not large enough to prevent interference and peak broadening. Nevertheless, Raman spectroscopy has been useful here to prove that chemical reactions have taken place on the surface of the electrodes.

3.2.5 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy, XPS, was also performed with the MOFs in situ on the glass IDEs. In this project it serves a similar role to EDX in that it is primarily used for element identification. The technique involves bombarding the sample with X-rays to stimulate emission of photoelectrons from deep core energy levels. The kinetic energy of these photoelectrons can be used to determine the binding energy of the level from which they came.¹⁸¹ This enables us to identify the elements present, but can also give us an insight into

the oxidation states of the atoms. Depending on the element in question, different oxidation states can give different binding energies, or lead to the presence of satellite peaks that are absent in the XPS spectrum of the atom in its neutral state. Such information about characteristic binding energies and satellite appearances is well documented in sources such as the Thermo Fisher Scientific XPS database.

To obtain the XPS data in this thesis, a K-alpha machine with an aluminium X-ray source was used (Thermo Scientific, USA). As photoelectrons are emitted during the measurements, positive ions are generated in the sample and charge can build up if it is not earthed properly. This is more common for samples with conductivities lower than those of typical metals, such as the MOFs in this project. In order to prevent this charge build up, an electron neutraliser beam was used.

3.3 Sensing techniques

Experiments in which sensing materials are exposed to analyte gases of particular concentrations will be referred to in chapters 4, 5 and 7 of this thesis. In section 3.3.1 the apparatus used to test the sensors' ability to detect different gaseous analytes will be described. The methods used to quantify the sensors' performances will be detailed in section 3.3.2.

3.3.1 Sensing chamber set-up

The apparatus used to expose the sensors to analyte gases comprises a sealed chamber with gas inlet and outlet and equipment for recording the sensing response. A power source is required to apply a constant voltage across the interdigitated electrodes, and a multimeter is needed to measure the current flowing. Gas flow controllers are connected to cylinders of the

desired analyte gases so that the relative flow rates of the analyte and carrier gases can be manipulated to control the analyte concentration. Such a set-up can be seen in Figure 3.7, whilst the layout within the gas sensing chamber (Figure 3.7 (e)) is depicted in Figure 3.8.¹⁸²

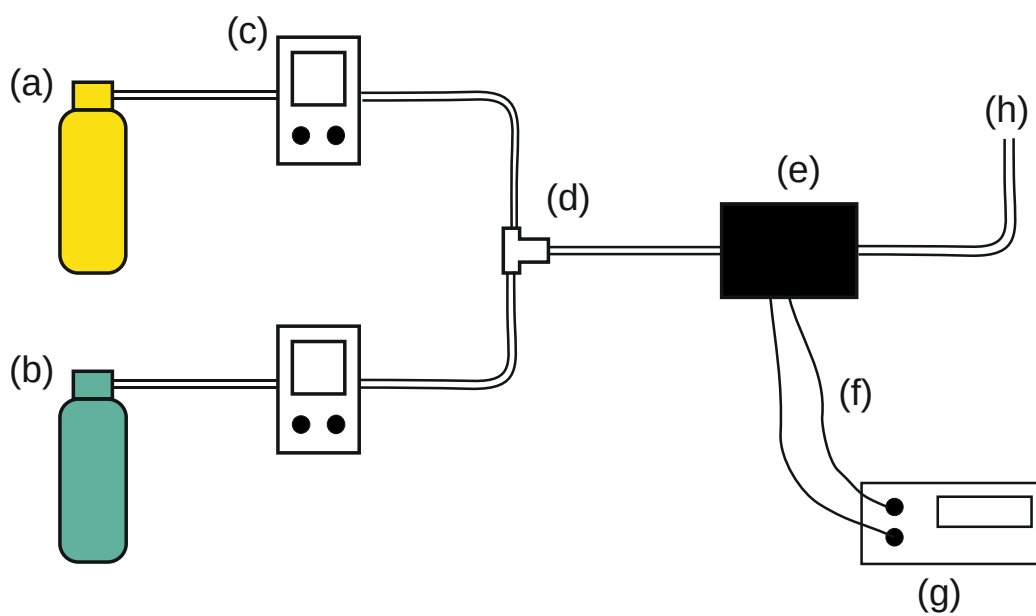


Figure 3.7: Schematic representation of the equipment used to measure the response of a chemiresistive sensor to analyte gases. (a) analyte gas cylinder (b) carrier gas cylinder (c) mass flow controller (d) T-junction to allow mixing of analyte and carrier gases (e) sensing chamber containing the sensor (f) wires connecting the sensor and multimeter (g) multimeter and power source (h) gas outlet.

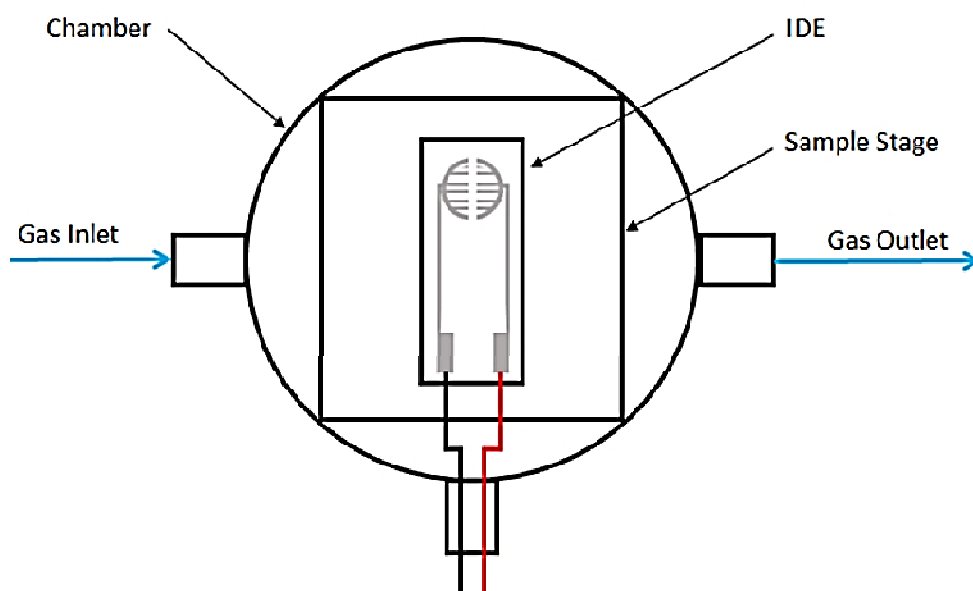


Figure 3.8: Schematic representation of the components inside the sensing chamber. The chamber is sealed except for gas inlet and outlets, and wires allowing for connection to the power supply and multimeter. The inter-digitated electrode sensor, IDE, is mounted on the sample stage over which the inlet gas will flow. A voltage is applied between the sides of the IDE using the power source, and a multimeter records the current flowing. The current changes as a function of analyte gas identity and concentration. Reproduced from reference 182.

For the work in this thesis, the gas cylinders used were both purchased from BOC gases, UK. The ammonia cylinder had an ammonia concentration of 10 ppm, diluted in dry nitrogen. The carrier gas was a zero-grade dry nitrogen. The gas flow from each cylinder was controlled using mass flow controllers purchased from Alicat Scientific, USA. The relative flow rates of gases from the two cylinders were controlled via a PC with FlowVision software, so that the ammonia gas concentration could be changed. The gas flows from each cylinder were mixed at a T-junction before entering the chamber. Inside the chamber, the sensor was connected to a U8001A Single Output DC Power Supply (Keysight, UK) to apply a potential of 1 V across the sensor, and to a B2900A Source Meter (Keysight, UK) to measure the current flowing. The current flow was monitored in real time on a PC with Keysight Benchvue software.

3.3.2 Sensor performance assessment

The primary quantitative factor used in literature to compare the success of sensors is their limit of detection, LOD. Whilst in practice the LOD of a sensor equates to the lowest concentration of analyte for which we observe a sensing response, the official IUPAC definition for a chemiresistor's LOD is the concentration that gives a response with magnitude equal to three times the standard deviation of the baseline resistance, or equivalently the root mean square of the baseline noise.¹⁸³ It is significant to note that the LOD is not usually directly measured through experiment, but calculated by extrapolation, as very low concentrations of analyte gases can often not be accurately obtained.

To calculate the LOD for a chemiresistive sensor, the response % for each gas exposure is first calculated using equation (1), where ΔR is the change in resistance on exposure and R_0 is the resistance before the exposure. The response for each exposure is then plotted against the concentration of gas in ppm. This plot should show response to linearly increase with concentration. The gradient of the best fit line is equal to the sensitivity of the sensor in % ppm⁻¹.

$$\text{Response \%} = \frac{\Delta R}{R_0} \times 100 \quad (1)$$

Statistically, it can be stated with over 99 % certainty that a signal with magnitude greater than 3 times the value of the baseline noise has not occurred through random fluctuations of the baseline signal.¹⁸³ In this vein the LOD in ppm can be calculated from the sensitivity through equation (2), where σ is the root mean square of the baseline noise. Further information

about the statistical justifications of this method can be found in the publication by Long et al.¹⁸³

$$\text{LOD} = \frac{3\sigma}{\text{sensitivity}}$$

(2)

Whilst the LOD and sensitivity are the most commonly quoted figures of merit for gas sensors, they are affected by a number of factors in addition to the analyte concentration. This means that the effectiveness of different sensors often cannot be meaningfully compared. For short analyte exposures where saturation of the sensor is not possible, the response magnitude has been found to be affected by the analyte exposure time.¹⁸⁴ It is also suspected that increasing the flow rate will increase the magnitude of the sensing response for a given concentration.¹⁸⁵ Until a mathematical way of correcting for flow rate in LOD calculations is developed, only sensors where the exposures were carried out at the same flow rate can have their LODs accurately compared. Moreover, the linear best-fit lines of the response vs concentration plots often do not pass through the origin. This means that in order for a 0 % response to register for a 0 ppm analyte exposure, there must be a deviation from the linear trend at concentrations below those sampled. Depending on how far the best fit line is extrapolated to calculate the LOD, this may introduce inaccuracies in the LOD value. In this project, the flow rate was kept constant at 500 sccm and analyte exposures were always 60 s in length.

Chapter 4

Synthesis and sensing performance of solution-synthesised MOFs

This chapter describes how the 4 structurally analogous $\text{Cu}_3(\text{HHTP})_2$, $\text{Cu}_3(\text{HITP})_2$, $\text{Ni}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HITP})_2$ MOFs were synthesised via solution synthesis and used to make sensors. The morphologies of the MOFs are assessed via SEM imaging and their crystal structures ascertained using PXRD. Their chemiresistive sensing responses to NH_3 and NO_2 gases are discussed and compared.

The sensing results in this chapter provide the benchmark to which the sensing performance of the MOF sensors made using the new synthesis methods described in chapters 6 and 7 can be compared. Moreover, by comparing the chemiresistive sensing response shapes of the solution synthesised MOFs, the role of the metal centre, ligand, MOF morphology and analyte gas on the sensing performance can be investigated. These experiments can give us an insight into the sensing mechanisms of the MOFs.

4.1 Context

In order for MOF sensors made by different methods to be accurately compared, a number of experimental conditions must be kept constant. These include the gas flow rate, carrier gas, exposure time to the analyte gas, whether the concentration is increased from a minimum or decreased from a maximum, voltage applied to the sensor, number of repeat exposures for each concentration, the size of the sensing chamber and the distance of the sensor from the gas inlet. The chemiresistive sensing responses of $\text{Cu}_3(\text{HHTP})_2$, $\text{Cu}_3(\text{HITP})_2$, $\text{Ni}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HITP})_2$ MOFs to oxidising and reducing gases have all been investigated and published

in literature, but the differing experimental conditions used make it difficult to decouple the effects of sensor fabrication/MOF synthesis methods from the effects of differing sensing conditions on sensor performance.

For the sensing results in this chapter, the same conditions are used throughout so that data given in subsequent chapters can be meaningfully compared. A voltage of 1.0 V is applied to all sensors, a dry N₂ carrier gas is used and the length of exposures to the analyte gases is always 60 s. An overall gas flow rate of 500 sccm is maintained throughout all the experiments. The same sensing chamber set-up is used, with the orientation and distance of the sensor from the gas inlet kept as constant as possible. It is common in literature for baselines to be corrected mathematically. In this chapter, the raw resistance changes before baseline correction are included to give a clear indication of the sensing response magnitude relative to any baseline changes.

NH₃ and NO₂ gases are the analytes used in the following experiments. By comparing the chemiresistive responses of the sensors to a reducing gas (NH₃) and an oxidising gas (NO₂) it may be possible to gain an insight into the sensing mechanisms taking place. The mechanistic insights will be summarised at the end of this chapter in section 4.4.

4.2 HHTP MOFs

The solution synthesis of Cu₃(HHTP)₂ and Ni₃(HHTP)₂ MOFs will be discussed in the following section, followed by SEM images depicting the crystal morphologies and characterisation of the MOFs with PXRD. In section 4.2.3, the chemiresistive sensing responses of the MOFs to NH₃ gas will be assessed, whilst the response to NO₂ gas will be discussed in section 4.2.4.

4.2.1 Synthesis

The $\text{Cu}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HHTP})_2$ MOFs were synthesised through heating solutions of the relevant metal salt and HHTP ligand as described in section 3.1.1. $\text{Cu}_3(\text{HHTP})_2$ MOF was synthesised from either copper trifluoroacetate, or copper nitrate trihydrate in the presence of 50 eq of ammonia. By synthesising the $\text{Cu}_3(\text{HHTP})_2$ MOF from different starting salts, samples of the same MOF with different crystal morphologies are produced. This means that the effect of morphology on sensing performance can be explored. In the remainder of this chapter, $\text{Cu}_3(\text{HHTP})_2$ synthesised from the copper trifluoroacetate salt will be referred to as $\alpha\text{-Cu}_3(\text{HHTP})_2$, whilst that synthesised from the copper nitrate trihydrate salt will be referred to as $n\text{-Cu}_3(\text{HHTP})_2$.

4.2.2 Characterisation

SEM was used to compare the morphologies of the $\text{Cu}_3(\text{HHTP})_2$ MOFs made from the different starting salts. At the top of Figure 4.1, crystals of $\alpha\text{-Cu}_3(\text{HHTP})_2$ synthesised from the trifluoroacetate starting salt are depicted, whilst below crystals of $n\text{-Cu}_3(\text{HHTP})_2$ synthesised from the nitrate starting salt are visible. Inspired by the work of Hoppe et al., the nitrate salt was selected to make the flatter crystals as the nitrate anion coordinates less strongly to the Cu^{2+} than the trifluoroacetate anion.¹⁶⁸ This means that other nitrogen-containing additives can more effectively modulate the crystal growth and dictate the morphology. 50 equivalents of aqueous ammonia were added to the copper nitrate trihydrate and HHTP synthesis solution. The theory behind this is that the ammonia molecules will occupy some of the coordination sites on the Cu^{2+} centres, preventing further reaction with the HHTP. The flake-like crystals visible in the SEM, Figure 4.1 – bottom, suggest that the presence of ammonia terminating groups inhibits stacking of the 2D MOF sheets, resulting in

flatter/thinner crystals.¹⁶⁸ It should also be noted that the crystals produced from the nitrate salt (Figure 4.1 – bottom) are shorter in length as well as flatter in width than the α - $\text{Cu}_3(\text{HHTP})_2$ crystals (Figure 4.2 – top). The effect of this larger surface area to volume ratio on the sensing performance will be discussed in sections 4.2.3 and 4.2.4.

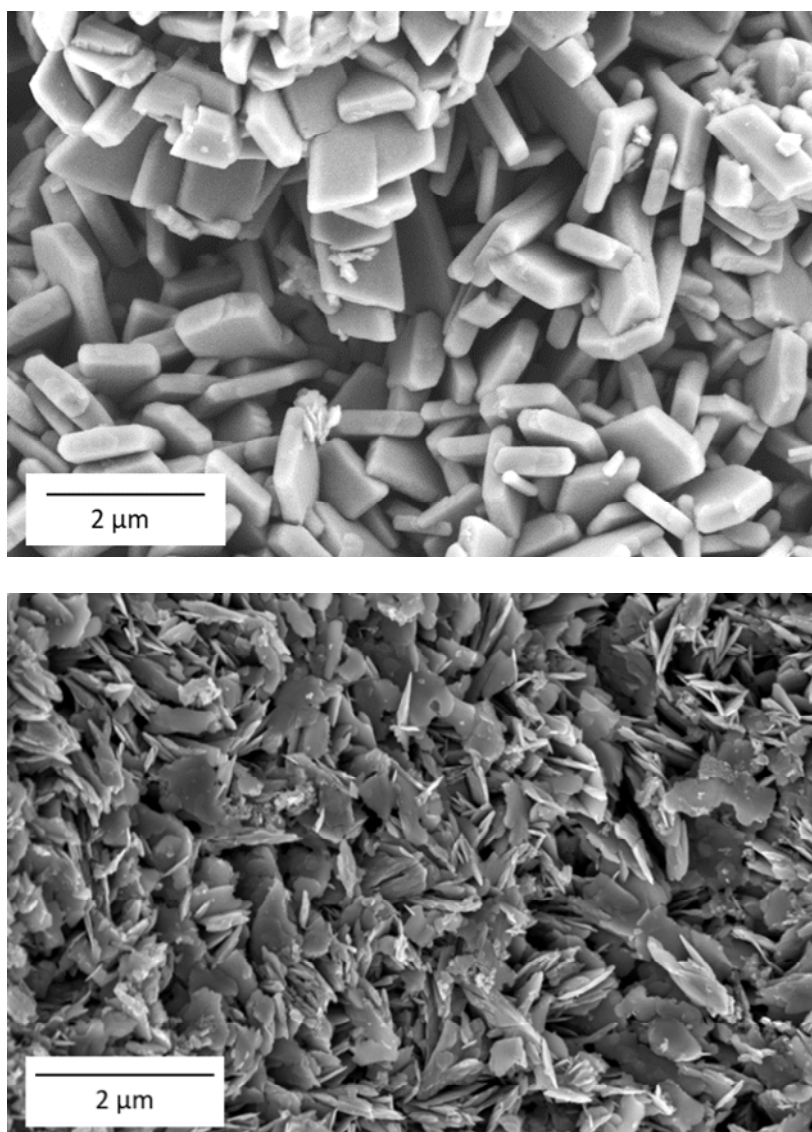


Figure 4.1: *Top* – SEM image of α - $\text{Cu}_3(\text{HHTP})_2$ synthesised from copper trifluoroacetate. *Bottom* – SEM image of n - $\text{Cu}_3(\text{HHTP})_2$ synthesised from copper nitrate trihydrate in the presence of 50 equivalents of ammonia. These crystals are flatter and smaller than those fabricated from the trifluoroacetate salt.

PXRD was used to confirm that the MOFs made from the two different methods were both $\text{Cu}_3(\text{HHTP})_2$, and a comparison of the relative peak heights was used to determine the

dimension which the ammonia additives affected the crystal growth. The PXRD data in Figure 4.2 shows that the peaks at $2\theta = 4.6^\circ$, 9.4° , 12.4° and 16.4° appear in the diffraction pattern for both $a\text{-Cu}_3(\text{HHTP})_2$ and $n\text{-Cu}_3(\text{HHTP})_2$. These can be indexed to the (100), (200), (210) and (220) planes respectively and correspond to lattice parameters a and b being equal to 22.2 Å. The peaks corresponding to stacking of the 2D crystals in the c -direction however differ slightly in position and shape between the $a\text{-Cu}_3(\text{HHTP})_2$ and $n\text{-Cu}_3(\text{HHTP})_2$ samples. In the $n\text{-Cu}_3(\text{HHTP})_2$ pattern the (001) peak appears at 28.2° corresponding to a lattice parameter, c , of 3.16 Å, whilst the analogous peak in the $a\text{-Cu}_3(\text{HHTP})_2$ pattern appears at 27.6° leading to a c value of 3.23 Å. This suggests that the presence of the ammonia modulator affects the interlayer spacing of the 2D MOF sheets, with the layers presenting slightly closer together on average in the ammonia-modulated crystals. However, the broadening of the (001) peak in the $n\text{-Cu}_3(\text{HHTP})_2$ sample increases the uncertainty in the reported 2θ value for this peak. This broadening could be due to slight stacking variations leading to a range of d_{001} values. However, the symmetrical nature of the peak makes Scherrer broadening due to the low thickness of the crystal in the c -direction the more logical conclusion. Calculation of the average particle thickness by using the full width half maximum in the Scherrer equation calculates the thickness to be 6 -7 nm, which is roughly consistent with the thickness observed in the SEM image at the bottom of Figure 4.1. The (001) peak in the $a\text{-Cu}_3(\text{HHTP})_2$ pattern is sharper, and other reflections in this region are visible. Comparison to simulated data suggests that the small peak at 29° corresponds to the (201) plane.¹⁶⁸

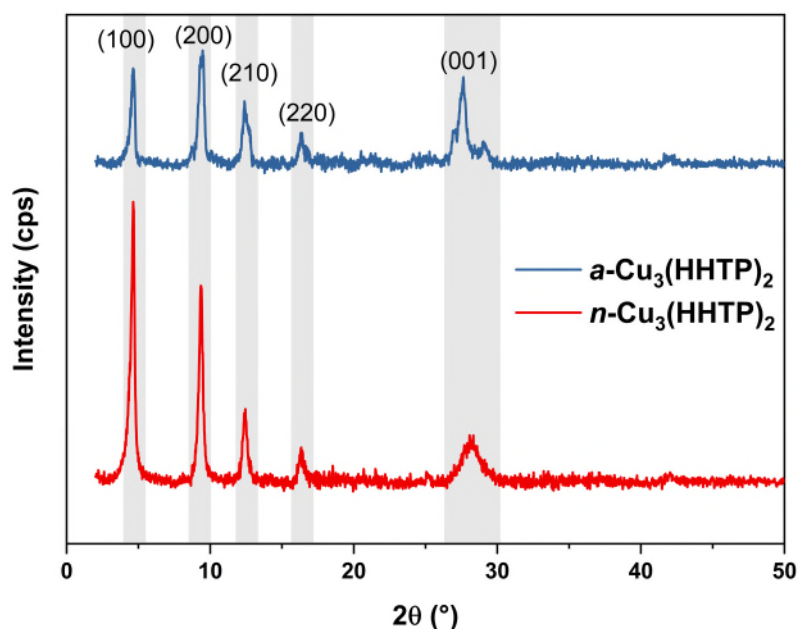


Figure 4.2: PXRD patterns for $a\text{-Cu}_3(\text{HHTP})_2$ synthesised from copper trifluoroacetate (**blue**) and $n\text{-Cu}_3(\text{HHTP})_2$ synthesised from copper nitrate trihydrate in the presence of 50 equivalents of ammonia (**red**). The (001), (200), (210), (200) and (001) peaks appear at very similar 2θ values, indicating that the MOFs have the same crystal structure.

The significantly reduced intensity of the (001) peak relative to the (100) peak in the $n\text{-Cu}_3(\text{HHTP})_2$ pattern compared to the same peaks in the $a\text{-Cu}_3(\text{HHTP})_2$ pattern, reflects the difference in morphologies of the samples observed in the SEM. It suggests that ordering in the c -direction is shorter range for the $n\text{-Cu}_3(\text{HHTP})_2$ MOF than for the $a\text{-Cu}_3(\text{HHTP})_2$ MOF. From this information it can be concluded that the pores' openings are present on the planes of the flakes. The effect of this on sensing performance will be looked at in section 4.2.3.

The structurally analogous $\text{Ni}_3(\text{HHTP})_2$ MOF was synthesised in aqueous solution as described in section 3.1.1. The resulting MOF crystals can be seen in the SEM image in Figure 4.3. This depicts rod-like crystals with hexagonal cross-sections.

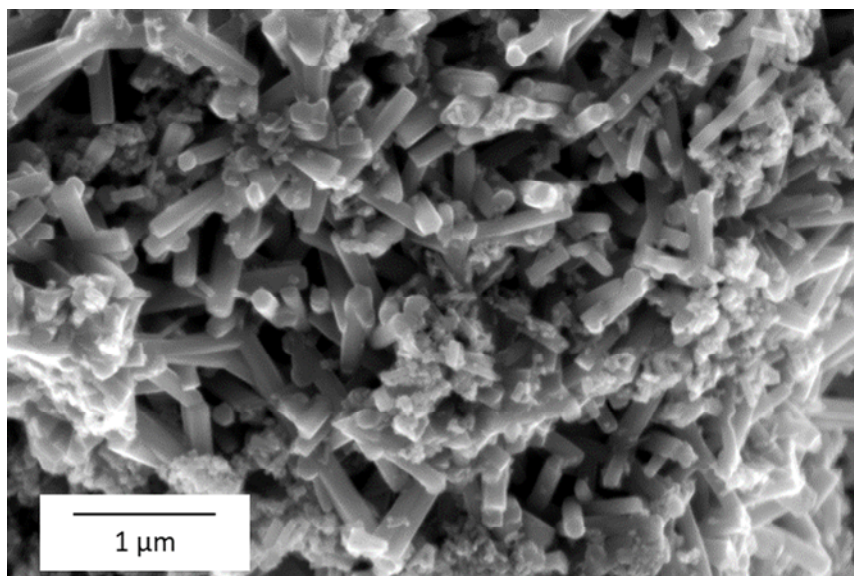


Figure 4.3: SEM image of $\text{Ni}_3(\text{HHTP})_2$ synthesised from a solution of the ligand and metal salt. Rod-like crystals with hexagonal cross sections are visible.

Further characterisation with PXRD reveals peaks at $2\theta = 4.6^\circ$, 9.3° , 12.3° and 16.1° , Figure 4.4. As for the $\text{Cu}_3(\text{HHTP})_2$ samples, these can be indexed to the (100), (200), (210) and (220) planes respectively. In contrast to the $\text{Cu}_3(\text{HHTP})_2$ patterns, the (001) peak appears at 13.9° , giving a c parameter of 6.36 Å, approximately double the c value for the analogous copper MOF. This is consistent with literature reports indicating that unlike the $\text{Cu}_3(\text{HHTP})_2$ MOFs which have slipped parallel AAAA stacking, the layers of the $\text{Ni}_3(\text{HHTP})_2$ MOF have an interpolated ABAB stacking arrangement.¹²⁰ As expected, this interpolated stacking arrangement would require a double height unit cell to describe the stacking periodicity of the crystal. The pattern obtained here is consistent with that published by Mirica et al., where they concluded the structure to be formed of 2D hexagonal sheets of MOF, interpolated with ordered layers of discrete hydrated $\text{Ni}_3(\text{HHTP})$ ions.¹⁴³ The likely effect of this stacking on the interaction of the MOF with analyte gases can be investigated by looking at the MOFs' chemiresistive responses to reducing and oxidising analyte gases.

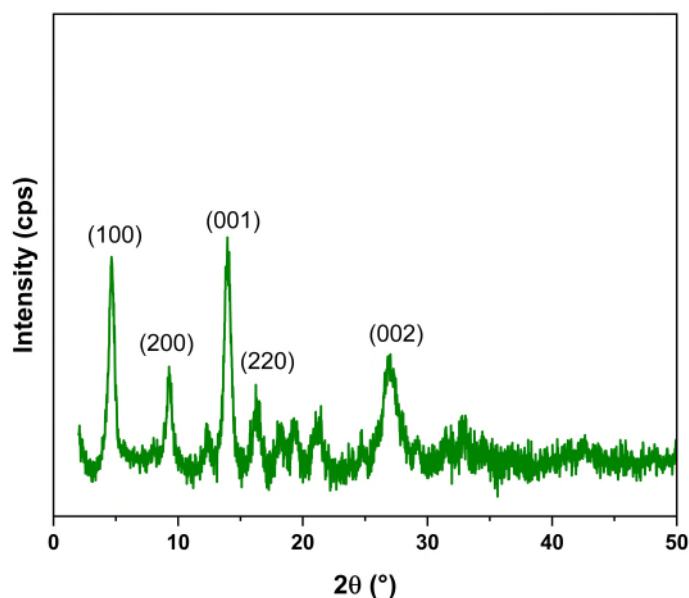


Figure 4.4: PXRD pattern of $\text{Ni}_3(\text{HHTP})_2$ MOF powder made via solution synthesis. Peaks corresponding to the (100), (200), (001), (220) and (002) planes have been indexed. The presence of two (00l) peaks indicates that the MOF is comprised of alternating layers.

4.2.3 Sensing response of HHTP MOFs to NH_3

Separate sensors were made from each of the $a\text{-Cu}_3(\text{HHTP})_2$, $n\text{-Cu}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HHTP})_2$ MOF powders. 10 mg mL^{-1} solutions of the MOFs were made up in IPA and $30 \times 5 \mu\text{L}$ droplets were drop-cast onto Pt/glass interdigitated electrodes (Micrux Technologies, Spain). The sensors were then submerged in acetone overnight before being removed and dried on a hot plate at 60°C for 20 minutes. The baseline resistance was allowed to settle for at least an hour before analyte exposures commenced. The $\text{Ni}_3(\text{HHTP})_2$ sensor showed no change in resistance on exposure to 5 ppm of NH_3 for 60 s, consistent with previously published studies.¹⁶⁴ Both $\text{Cu}_3(\text{HHTP})_2$ sensors did respond to 60 s exposures of NH_3 gas with concentrations between 5 ppm and 1 ppm. The results of these experiments can be seen in Figure 4.5.

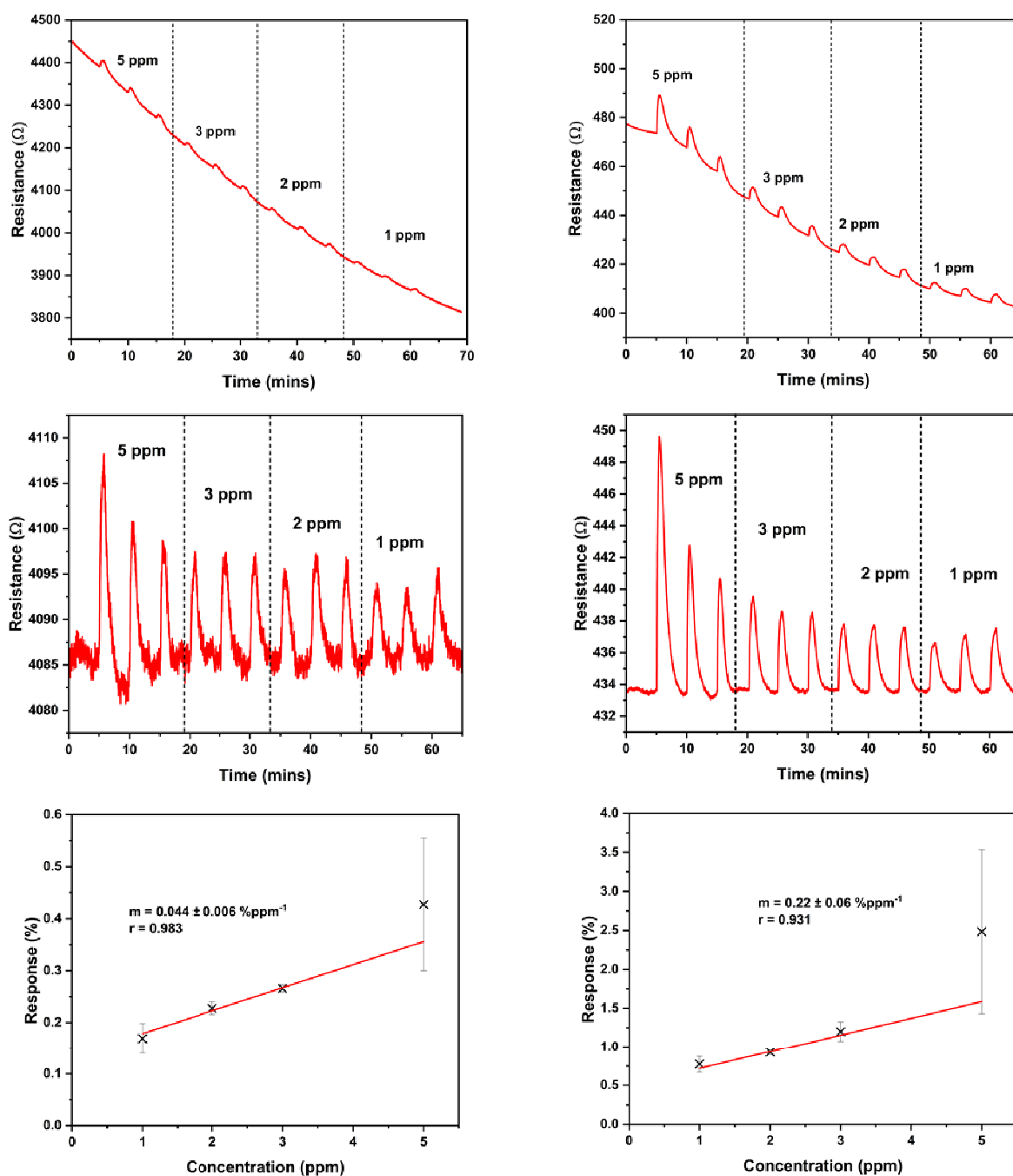


Figure 4.5: **Top Left** - Resistance change of an $a\text{-Cu}_3(\text{HHTP})_2$ sensor exposed to NH_3 gas with concentrations between 5 and 1 ppm. **Centre Left** - Baseline corrected resistance change of the $a\text{-Cu}_3(\text{HHTP})_2$ sensor exposed to NH_3 gas. **Bottom Left** - Corresponding calibration plot for the $a\text{-Cu}_3(\text{HHTP})_2$ response to NH_3 . **Top Right** - Resistance change of an $n\text{-Cu}_3(\text{HHTP})_2$ sensor exposed to NH_3 gas with concentrations between 5 and 1 ppm. **Centre Right** - Baseline corrected resistance change of the $n\text{-Cu}_3(\text{HHTP})_2$ sensor exposed to NH_3 gas. **Bottom Right** - Resistance change of the $n\text{-Cu}_3(\text{HHTP})_2$ sensor exposed to NH_3 gas. Both sensors respond with reversible resistance increases when exposed to NH_3 gas, but the sensitivity of the sensor fabricated from the flatter $n\text{-Cu}_3(\text{HHTP})_2$ crystals is superior.

By inspecting the raw resistance change plot shown on the top left of Figure 4.5 for an *a*-Cu₃(HHTP)₂ sensor and the top right for an *n*-Cu₃(HHTP)₂ sensor, a significant baseline resistance decrease can be seen for both sensors. This could be due to the dry N₂ carrier gas flow driving off any residual solvent molecules that could be present adhered to the IDEs or inside the MOF pores themselves. The resistance decrease persists after many hours of dry N₂ flow which implies that it is likely to be solvent inside the MOF that is being drawn out, rather than solvent adhered to the electrode surface. The increase in current whilst a continuous voltage is maintained implies that the solvent molecules, (water, IPA and acetone were all used in the synthesis) interact with the MOF in a way that reduces its conductivity. On exposure to the reducing gas, NH₃, the resistance of both Cu₃(HHTP)₂ sensors increased reversibly. Since it is suspected that residual solvent increases the resistance too, this could mean that the same sites on the MOF can be occupied by solvent and reducing gas molecules. The fact that the analogous Ni₃(HHTP)₂ MOF did not respond to NH₃ gas suggests that the interaction site is likely on the Cu centre.

Comparison of the plots at the top of Figure 4.5 reveals that the *n*-Cu₃(HHTP)₂ sensor gives resistance increases with magnitudes much larger relative to the baseline drift than the *a*-Cu₃(HHTP)₂ sensor does. By subtracting a baseline formed from interpolating between the points on the curve just before analyte exposure, and then adding the average resistance of this baseline, the baseline-corrected plots in the centre of Figure 4.5 are obtained.

The change in resistance as a percentage of the initial resistance (the response) is calculated for each analyte exposure and a plot of the response % against concentration for each sensor can be seen at the bottom of Figure 4.5. The gradient of these calibration plots gives the sensitivities of the sensor. The sensitivity of the *n*-Cu₃(HHTP)₂ sensor is found to be 5 times higher than the *a*-Cu₃(HHTP)₂ at $0.22 \pm 0.06 \text{ \% ppm}^{-1}$ compared to $0.044 \pm 0.006 \text{ \% ppm}^{-1}$.

Using the sensitivities derived from the calibration plots, theoretical limits of detection can be

calculated. The noisier baseline and smaller response percentages gave the α -Cu₃(HHTP)₂ sensor a higher LOD of 1.2 ± 0.2 ppm, whilst the LOD for the n -Cu₃(HHTP)₂ sample was calculated to be 0.12 ± 0.03 ppm. For an ideal sensor, the best fit line of the calibration plot should pass through the origin, indicating that an analyte concentration of 0 would give a 0 % response. However, this is rarely the case for chemical sensors like MOFs and is not the case for the plots in Figure 4.5. The offset of the best fit line from the origin means that the response vs concentration behaviour must deviate from the linear trend at very low concentrations. As the intercepts of the best fit lines are positive however, the gradients must increase as the concentration decreases to below 1 ppm, leading to higher sensitivities in the low concentration region.

The superior sensing ability of the n -Cu₃(HHTP)₂ sample implies that the flake-like particle morphology and/or smaller particle dimensions are favourable for generating NH₃ sensors in terms of response magnitude. This is likely due to the greater proportion of pores exposed at the surface of the particles, reducing the distance an analyte molecule must diffuse before reaching a site to bind to on the MOF. The measured conductivity across the IDEs for the same mass of MOF was also higher for the n -Cu₃(HHTP)₂ sensor suggesting that there is better electrical contact between the particles. Furthermore, the baseline drift of the n -Cu₃(HHTP)₂ was also less significant. Whether the same enhanced sensing response for the MOF with the flake-like morphology is observed when the sensors are exposed to NO₂ gas will be discussed in the following section.

4.2.4 Sensing response of HHTP MOFs to NO₂

All three of the α -Cu₃(HHTP)₂, n -Cu₃(HHTP)₂ and Ni₃(HHTP)₂ MOF sensors were found to respond to NO₂ gas giving irreversible resistance decreases, Figure 4.6. The contrasting

magnitude and reversibility of the responses to NO₂ and NH₃ imply that a different sensing mechanism is taking place, likely at a different site on the MOF, with a suggestion that the NO₂ remains permanently chemically bound to the framework. The largely irreversible nature of the responses means that the magnitude of subsequent sensing responses is highly dependent on the number of prior analyte exposures. As such, exposures at each concentration were not repeated and no calibration plot could be obtained. Instead, the change in resistance as a percentage of the initial resistance for 5 ppm exposures for each sensor are compared. The highest percentage change in resistance was for the α -Cu₃(HHTP)₂ sensor at 19.6 % followed by the Ni₃(HHTP)₂ sensor at 17.0 %. At 8.7 % the n -Cu₃(HHTP)₂ sensor gave the smallest resistance decrease. This suggests that the accessibility of the pores does not limit the response magnitude when it comes to interaction with NO₂ gases. The fact that the same type of response is seen when both Ni and Cu-based HHTP sensors are exposed to NO₂ gas suggests that the NO₂ is not binding to the metal centres, and is more likely to participate in an irreversible chemical interaction with the ligand. The contrasting ABAB stacking mode of the Ni₃(HHTP)₂ MOF compared the Cu₃(HHTP)₂ MOF's AAAA stacking does not appear to affect the sensing response to NO₂, despite the fact that the resulting sensor has a significantly higher initial resistance. This Ni₃(HHTP)₂ sensor does however have a higher baseline noise than the analogous Cu sensors. If reversible responses were observed, this would result in a significantly higher calculated LOD.

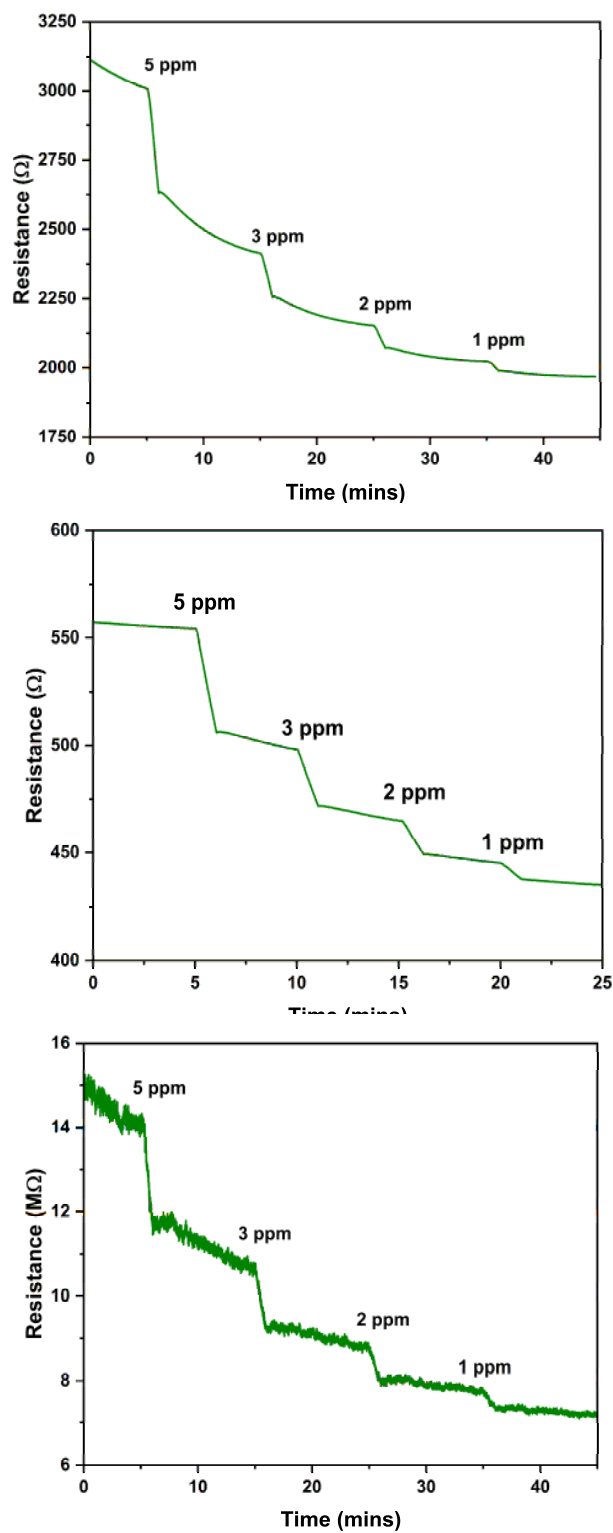


Figure 4.6: Resistance changes of α -Cu₃(HHTP)₂ (top), n -Cu₃(HHTP)₂ (centre) and Ni₃(HHTP)₂ (bottom) sensors to concentrations of NO₂ gas between 5 and 1 ppm. All sensors show irreversible resistance decreases on exposure to NO₂.

4.3 HITP MOFs

Analogous MOFs made from hexa-substituted triphenylene molecules with amine groups rather than hydroxyl groups were also synthesised. In this section solution synthesis routes to produce these MOFs will be discussed, followed by how they were characterised by SEM and PXRD. Their sensing responses to NH_3 and NO_2 analyte gases will then be explored.

4.3.1 HITP MOF synthesis

Both MOFs were synthesised using the experimental protocols outlined in section 3.1.1. A nickel(II) acetate trihydrate salt was used for synthesis of $\text{Ni}_3(\text{HITP})_2$ and synthesis of the $\text{Cu}_3(\text{HITP})_2$ MOF was only attempted from the copper(II) acetate salt. The organic starting material used was 2,3,6,7,10,11-hexamine triphenylene in its hexahydrochloride form. The sensors were fabricated using the same protocol as for the HHTP sensors, where 10 mg mL^{-1} solutions of the MOFs were made up in IPA and $30 \times 5 \text{ }\mu\text{L}$ droplets were drop-cast onto Pt/glass interdigitated electrodes (Micrux Technologies, Spain). The sensors were then submerged in acetone overnight before being removed and dried on a hot plate at 60°C for 20 minutes.

4.3.2 HITP MOF characterisation

The morphologies of the $\text{Cu}_3(\text{HITP})_2$ and $\text{Ni}_3(\text{HITP})_2$ MOFs were investigated using SEM to produce the images in Figure 4.7. Both images depict densely packed microcrystallites with dimensions smaller than $1 \text{ }\mu\text{m}$. This is in contrast to the HHTP MOFs depicted in Figure 4.1 where the crystals were typically at least $1 \text{ }\mu\text{m}$ in one dimension.

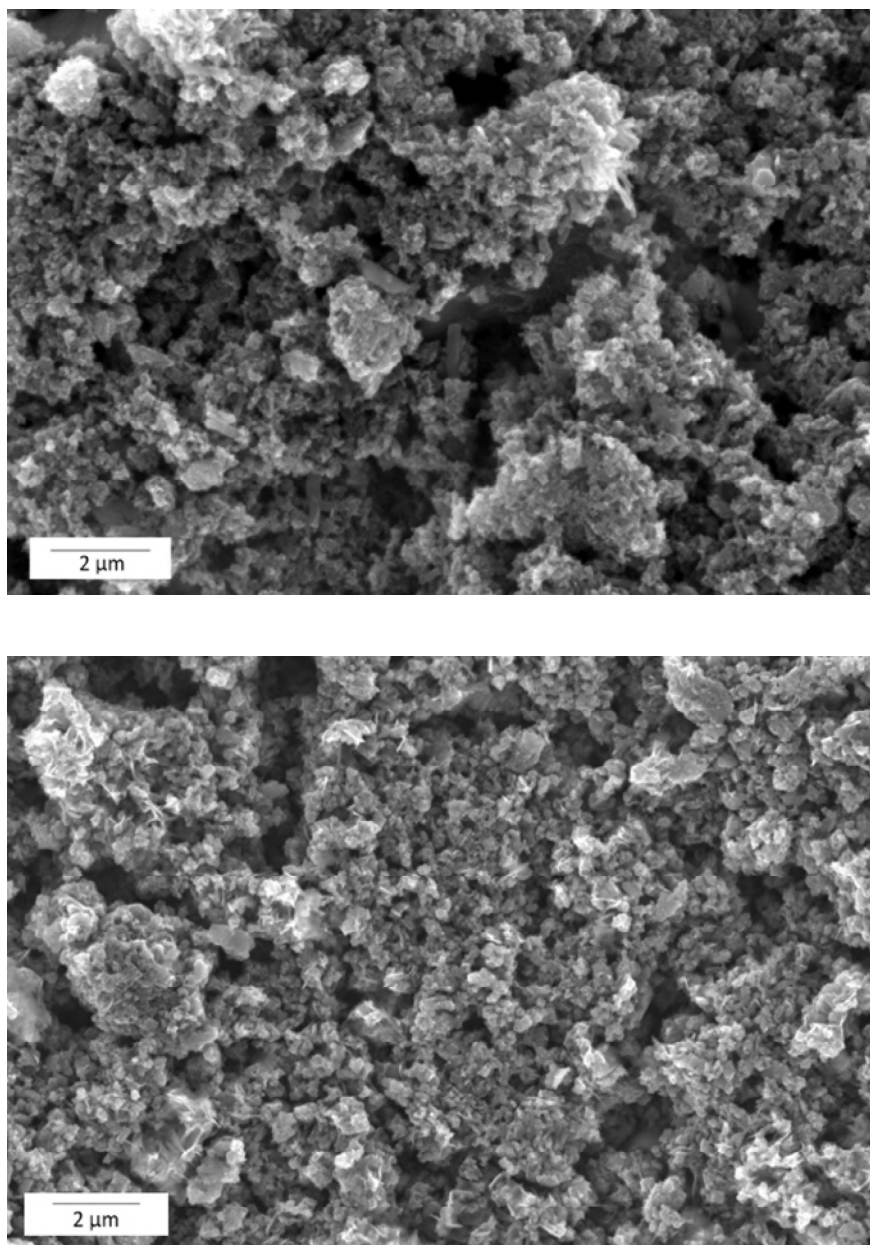


Figure 4.7: *Top* - SEM image of $\text{Cu}_3(\text{HITP})_2$ synthesised via solution synthesis. *Bottom* - SEM image of $\text{Ni}_3(\text{HITP})_2$ synthesised via solution synthesis. Both MOF samples depict densely packed microcrystallites with smaller dimensions than the analogous HHTP-based MOFs.

Further characterisation by PXRD revealed a similar crystal structure to the $\text{Cu}_3(\text{HHTP})_2$ MOFs referred to in section 4.2. For the $\text{Cu}_3(\text{HITP})_2$ PXRD trace depicted in Figure 4.8 (red), peaks at $2\theta = 4.8^\circ, 9.5^\circ, 12.4^\circ, 17.0^\circ$ and 27.9° are observed. When indexed to a hexagonal unit cell these can be assigned to the (100), (200), (210), (220) and (001) planes respectively. Similarly, peaks are observed in the $\text{Ni}_3(\text{HITP})_2$ trace, Figure 4.8 (black), at $2\theta = 5.0^\circ, 9.5^\circ,$

12.9° and 27.3° which can be indexed to the (100), (200), (210) and (001) planes. For the $\text{Cu}_3(\text{HITP})_2$ MOF these peaks correspond to lattice parameters $a = 21.1 \text{ \AA}$ and $c = 3.2 \text{ \AA}$, whilst for the $\text{Ni}_3(\text{HITP})_2$ MOF the calculated values were $a = 20.4 \text{ \AA}$ and $c = 3.3 \text{ \AA}$. Both PXRD traces are consistent with the MOFs having slipped parallel AAAA layer stacking. Also observable in the $\text{Ni}_3(\text{HITP})_2$ trace, marked with asterisks, are peaks at $2\theta = 19.4^\circ$, 33.3° and 38.7° . These are consistent with peaks expected for $\text{Ni}(\text{OH})_2$,¹⁸⁶ indicating that this has formed in addition to the desired MOF. No additional base was added to the solution but the presence of the basic acetate coordinating anion is likely responsible for this. Some $\text{Cu}(\text{OH})_2$ may also have formed during the analogous Cu MOF synthesis, but the higher solubility of this hydroxide means that it will have been removed at the filtration stage whilst the $\text{Ni}(\text{OH})_2$ persists.

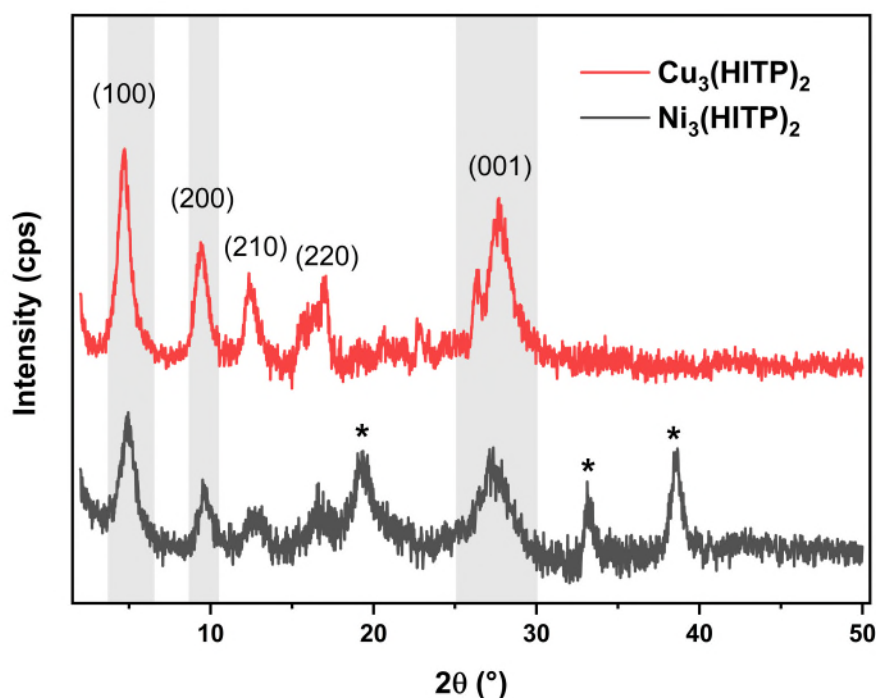


Figure 4.8: PXRD patterns for solution synthesised $\text{Cu}_3(\text{HITP})_2$ (red) and $\text{Ni}_3(\text{HITP})_2$ (black). The (100), (200), (210) and (001) peaks appear at similar 2θ values for both MOFs, indicating that they have the same crystal structure. Peaks corresponding to $\text{Ni}(\text{OH})_2$ are marked with asterisks.

4.3.3 Sensing response of HTP MOFs to NH₃

As was the case for the analogous HHTP MOF, the Cu₃(HTP)₂ MOF responded to NH₃ gas exposures with reversible resistance increases, Figure 4.9 – top. Again the baseline resistance is observed to decrease throughout the experiment, and for many hours before the analyte gas exposures were started. The same baseline correction procedure as described in section 4.2.3 was performed to produce the plot depicted in the centre of Figure 4.9. Plotting the change in resistance on exposure to NH₃ as a percentage of the original resistance enables the calibration plot at the bottom of Figure 4.9 to be obtained. The sensitivity of the sensor was extracted from the gradient of the plot to give a value of $0.052 \pm 0.006 \text{ \% ppm}^{-1}$. This correlates to a theoretical limit of detection of $0.53 \pm 0.06 \text{ ppm}$. This is intermediate between the LODs of the *a*-Cu₃(HHTP)₂ and *n*-Cu₃(HHTP)₂ sensors described in section 4.2.3. The similar response shapes and limits of detection for the Cu HHTP and HTP MOF sensors makes it likely that the same sensing mechanism takes place when both Cu MOFs are exposed to NH₃.

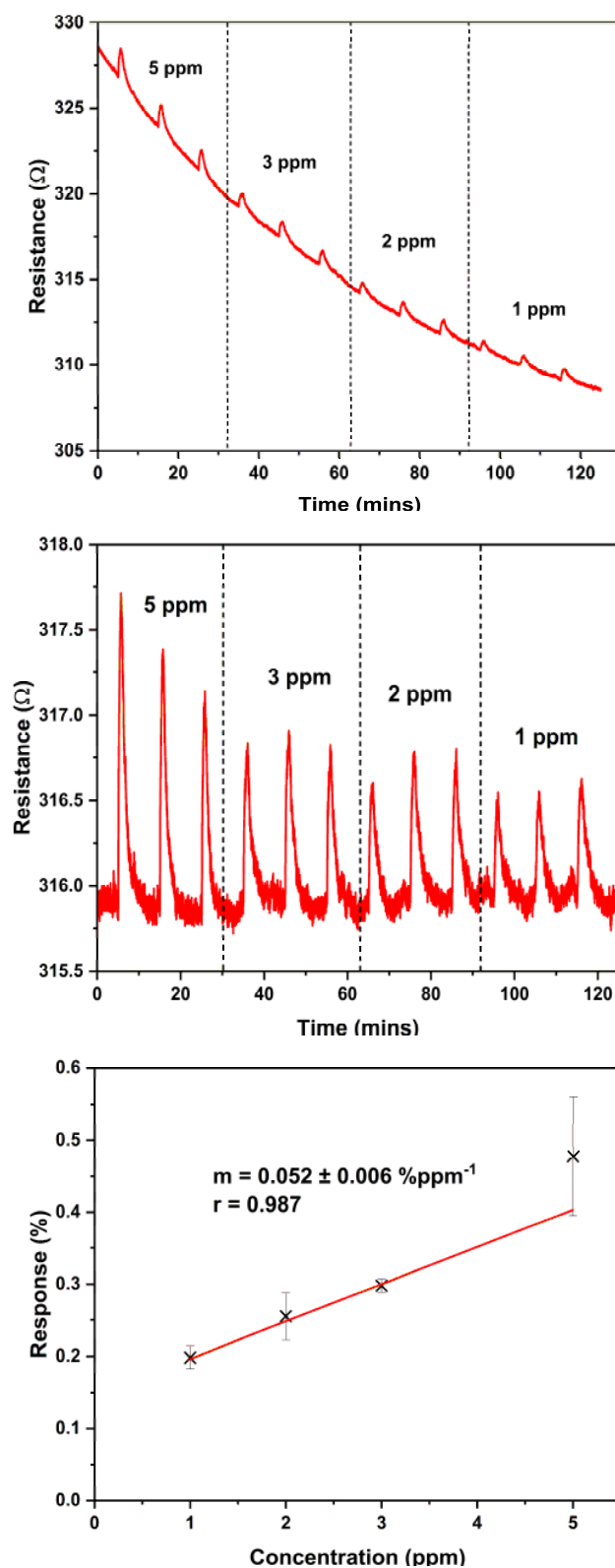


Figure 4.9: *Top* - Resistance change of a $\text{Cu}_3(\text{HITP})_2$ sensor exposed to NH_3 gas with concentrations between 5 and 1 ppm. *Centre* - Baseline-corrected resistance change of the $\text{Cu}_3(\text{HITP})_2$ sensor exposed to NH_3 gas. *Bottom* - Corresponding calibration plot for $\text{Cu}_3(\text{HITP})_2$ response to NH_3 .

Like the $\text{Ni}_3(\text{HHTP})_2$ sensors, sensors made from $\text{Ni}_3(\text{HITP})_2$ did not respond to NH_3 gas. Again this suggests that the NH_3 interaction is taking place at the Cu centre or via another mechanism that is precluded in the $\text{Ni}_3(\text{HITP})_2$ MOF. Further discussion of likely mechanisms of interaction between the frameworks and the analyte gases will be given in section 4.4.

4.3.4 Sensing response of HITP MOFs to NO_2

The raw resistance change on exposure of a $\text{Cu}_3(\text{HITP})_2$ MOF sensor to NO_2 gas is depicted in Figure 4.10 – top. In this figure we see a non-linear background resistance change. Subtracting a baseline formed from interpolating between the points just before each analyte exposure, then adding the average pre-exposure resistance results in the plot displayed in the centre of Figure 4.10. Plotting the average percentage change in resistance for each exposure concentration produces the plot at the bottom of Figure 4.10. The gradient of this plot gives a sensitivity to NO_2 exposure of $0.05 \pm 0.01 \text{ \% ppm}^{-1}$, with a Pearson's r value of 0.9813 for the linear fit. From this a limit of detection of $1.1 \pm 0.2 \text{ ppm}$ is calculated. Whilst the sensing performance is non-ideal in terms of the high error in the LOD, relatively poor linearity in the concentration vs response plot, and fluctuating baseline, this sensor does provide the only reversible response to NO_2 of the MOF sensors described in this chapter. Should further $\text{Cu}_3(\text{HITP})_2$ MOF sensors made by the novel methods described in this thesis offer improvements with respect to the above limitations, this would therefore provide an important advancement in terms of NO_2 sensing. Potential reasons as to why this MOF in particular responds reversibly to NO_2 , whilst the others respond irreversibly or not at all, will be discussed in section 4.4.

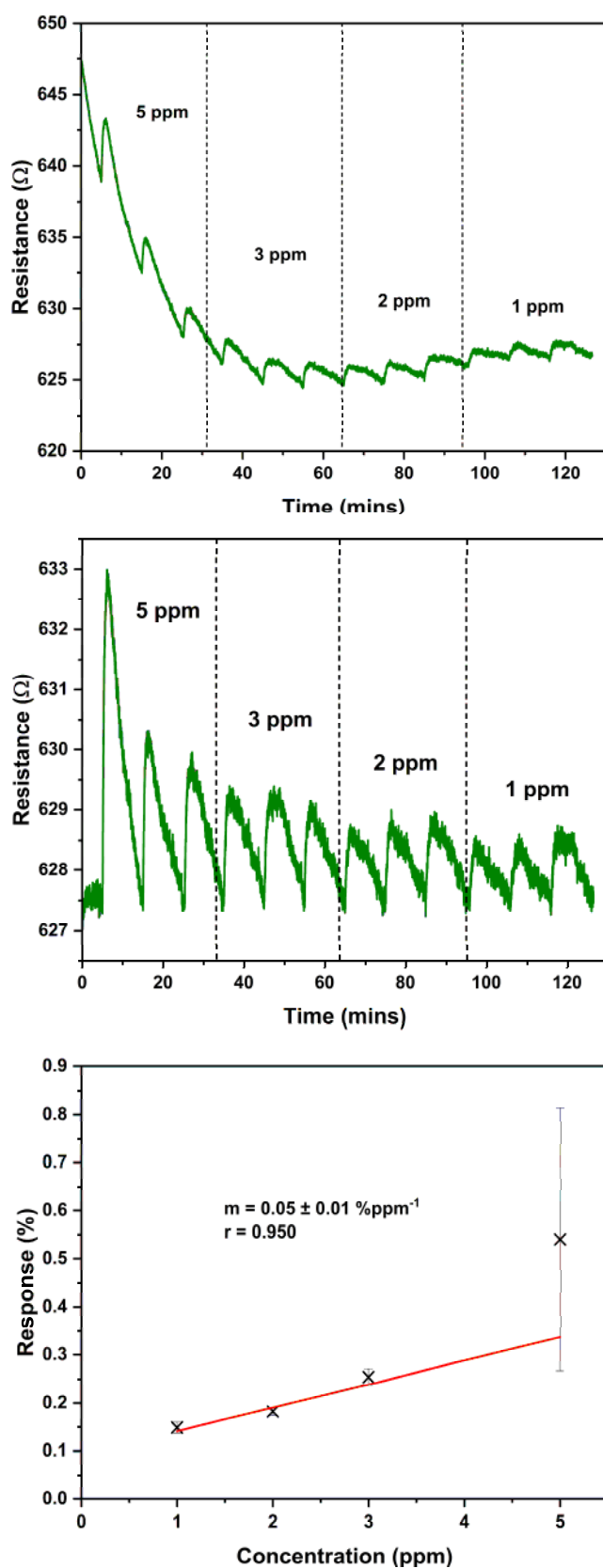


Figure 4.10: *Top* - Resistance change of a $\text{Cu}_3(\text{HITP})_2$ sensor exposed to NO_2 gas with concentrations between 5 and 1 ppm. *Centre* - Baseline-corrected resistance change of the $\text{Cu}_3(\text{HITP})_2$ sensor exposed to NO_2 gas. *Bottom* - Corresponding calibration plot for $\text{Cu}_3(\text{HITP})_2$ response to NO_2 .

The $\text{Ni}_3(\text{HITP})_2$ MOF did not respond to exposures of NO_2 gas, despite the conductivity of the sensors produced being the highest of those discussed in this chapter (of the order of 100 Ω). It could therefore be that any changes in conductivity due to analyte interaction have little impact on the measured current flow due to the high abundance of other conductive pathways.

4.4 Sensing mechanisms

Throughout this chapter the effects of two different analyte gases on the conductivity of 4 different MOFs have been investigated. Finding sensing mechanisms to explain all of the interactions is not a trivial task, but insight can be gleaned from the sensing responses, theoretical calculations and various analytical techniques. The 4 MOFs surveyed have similarities and differences in terms of ligand, metal centre, stacking mode and morphology, whilst the NH_3 and NO_2 analyte gases differ in their redox properties. NH_3 is considered a reducing gas containing a lone pair of electrons in an sp^3 hybrid orbital, enabling it to act as a Lewis base. On interaction with a p-type semiconductor, we would therefore anticipate the resistance to increase. Contrastingly, NO_2 is an oxidising gas which can act as a Lewis acid by accepting electrons to the positively charged N centre of the zwitterionic molecule, as exemplified in Figure 4.11. We would therefore anticipate the interaction of NO_2 with a p-type semiconductor to increase the resistance.

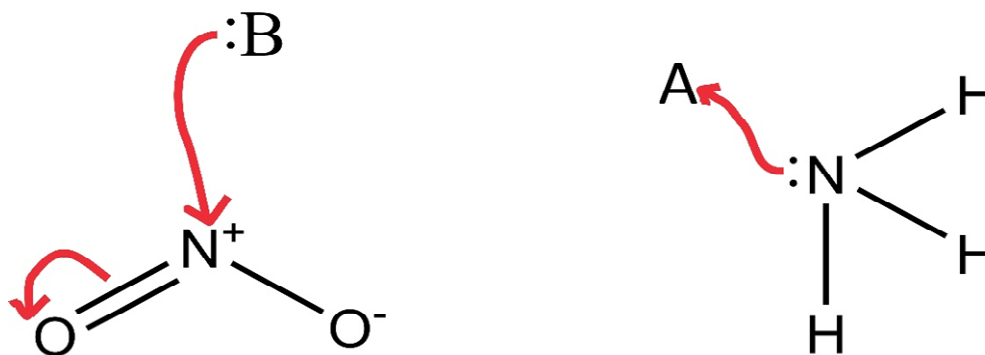


Figure 4.11: *Left* – Interaction between NO_2 analyte gas and a base, B. The NO_2 molecule accepts a lone pair of electrons from the base. *Right* – Interaction between NH_3 and an acid, A. The NH_3 molecule donates a pair of electrons to the acid.

The resistance responses of the 4 surveyed MOFs on exposure to NH_3 and NO_2 analyte gases explored earlier in this chapter are summarised in Figure 4.12. A reversible resistance increase on exposure to NH_3 occurred for Cu MOFs with either HHTP or HITP ligands but not for either of the Ni-based MOFs, suggesting that the Cu-centre is the likely site for NH_3 interaction. This supports the conclusions made by Rubio-Giménez et al. and Mirica et al., as discussed in section 2.6, which identify the Cu site as the site of interaction with NH_3 . This resistance increase is consistent with the $\text{Cu}_3(\text{HHTP})_2$ MOF acting as a p-type semiconductor, whereby the NH_3 donates electron density to the framework, reducing the concentration of holes and consequently increasing the resistance. There may also be a contribution to the resistance increase made by the NH_3 distorting the planarity at the Cu centres, and so pushing the 2D layers apart and reducing through-space charge transport as theorised by Rubio-Giménez et al.¹⁴⁴ The reversible nature of the resistance response suggests that a short-lived charge carrier doping interaction is taking place rather than a permanent chemical change. It could be that the NH_3 -induced lattice distortions introduce some strain into the MOF crystals, making it reasonable to assume that an NH_3 concentration dependant equilibrium is set up in which favourable Cu- NH_3 interactions compete with strain-induced desorption.

MOF	Response to NH ₃
Cu ₃ (HHTP) ₂	Reversible resistance increase
Cu ₃ (HITP) ₂	Reversible resistance increase
Ni ₃ (HHTP) ₂	No response
Ni ₃ (HITP) ₂	No response

MOF	Response to NO ₂
Cu ₃ (HHTP) ₂	Irreversible resistance decrease
Cu ₃ (HITP) ₂	Reversible resistance increase
Ni ₃ (HHTP) ₂	Irreversible resistance decrease
Ni ₃ (HITP) ₂	No response

Figure. 4.12: Top – Summary of the resistance responses of the MOFs featured in this chapter to NH₃ gas. **Bottom** – Summary of the resistance responses of the MOFs featured in this chapter to NO₂ gas.

The absence of a response of the analogous Ni MOFs to NH₃ is consistent with literature reports and is as expected considering the inflexible valency of Ni ions. Whilst both Cu⁺ and Cu²⁺ ions are stable, Ni⁺ is not stable so reducing Ni²⁺ to Ni⁺ would not be feasible. This is reflected in the lack of evidence for redox communication between the ligands and Ni ion centres as found through the experiments performed by Stolz et al.¹⁴³ described in section 2.6.

The resistance decreases of the Cu₃(HHTP)₂ and Ni₃(HHTP)₂ to NO₂ is what we would expect from a p-type semiconductor interacting with an oxidising gas. The NO₂ gas can withdraw electron density from the framework, increase the concentration of holes and therefore decrease the resistance. In the work published by Jo et al. on Cu₃(HHTP)₂/Fe₂O₃ hybrids, the authors concluded that the NO₂ gas was interacting at the Cu centres.¹⁶⁷ However, in this chapter it has been shown that the same shape of resistance response is observed when both Ni and Cu HHTP based MOFs are exposed to NO₂, whilst different/no responses are observed for Ni and Cu MOFs with HITP ligands. This suggests that it is more likely that the NO₂ gas is interacting via the HHTP ligands. Moreover, the irreversible nature of the HHTP MOF and

NO₂ interactions implies a very different type of interaction is occurring to that which was observed for the NH₃ analyte.

The fact that the same irreversible decrease is observed for both the Ni and Cu HHTP MOFs suggests that the ligand plays a key role in the interaction. In both the HHTP and HITP based MOFs, the heteroatoms involved in bonding to the metal are considered to be sp² hybridised with approximately trigonal planar geometry. For the HITP MOFs, the N atoms donate one lone pair of electrons to the π -system above and below the plane, and then participate in 3 in-plane bonds to the metal, a carbon from the ligand, and also to a hydrogen atom. Each O atom in the HHTP-based ligands similarly donates one lone pair of electrons to the π -system, and participates in an in-plane bond to the metal and a carbon from the ligand. However, instead of forming a third in-plane bond to a hydrogen atom as occurred for the HITP analogue, the final sp² hybrid orbital is occupied by a lone pair of electrons. It is this pendant lone pair from the oxygen that we suspect to be the site for interaction with the NO₂ gas.

This pendant lone pair gives an opportunity for NO₂ to interact with the ligand in the plane of the MOF layers. A potential route for this is sketched in Figure 4.13. Interaction in this plane via the ligand would not lead to the layers being pushed apart as was the case for the NH₃ interaction mechanism, and would therefore not result in disruption to the through-space charge transport pathway. If better quality crystals of the MOFs after permanent interaction with NO₂ could be obtained, the location of the NO₂ could potentially be confirmed via SCXRD. Co₃(HHTP)₂ could be a promising candidate for this as prior success has been reported in literature in obtaining single crystal data for this MOF,¹⁴¹ but the Ni₃(HHTP)₂ and Cu₃(HHTP)₂ crystals are typically too small for such experiments to be carried out.

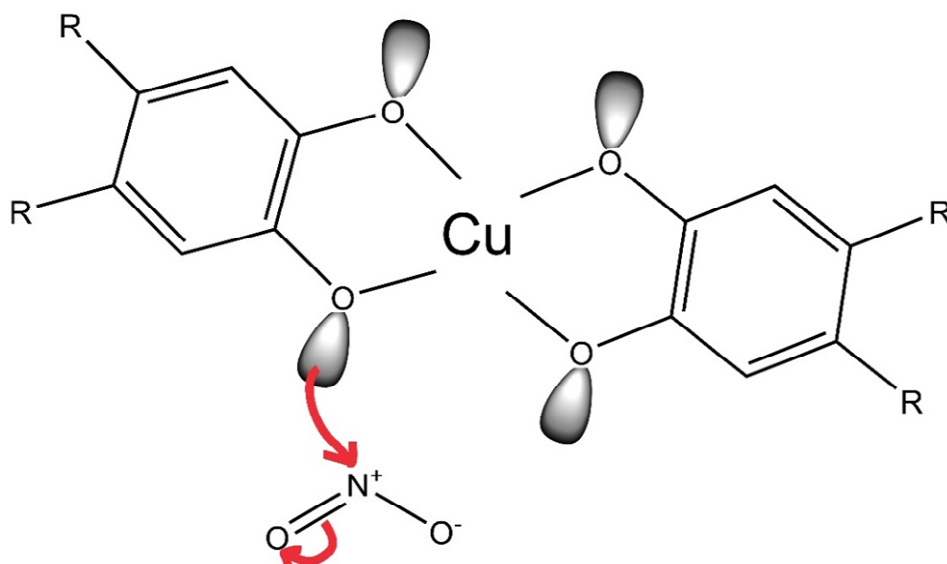


Figure 4.13: Schematic illustration of how an oxygen lone pair can interact with an NO_2 analyte, within the plane of the MOF layers. This interaction involves withdrawal of electrons from the conjugation plane, increasing the conductivity of a p-type semiconductor.

The reversible resistance increase observed when $\text{Cu}_3(\text{HITP})_2$ is exposed to NO_2 is initially surprising given the typical classification of $\text{Cu}_3(\text{HITP})_2$ as a p-type semiconductor. However, on closer inspection we see that $\text{Cu}_3(\text{HITP})_2$ is the only MOF which Mirica et al. found to have redox communication between metal and ligand, in which charge is preferentially stored on the metal rather than ligand in its interaction with NH_3 . By this logic, if NO_2 interacts at the metal centre, likely removing electron density from Cu^+ ions, electrons can be transferred from the ligand to the metal to stabilise the interaction. In a simple semiconductor model of the MOF, we would anticipate this interaction to reduce the resistance. However, if the disruption to the through-space transport due to distortion of the planarity at the metal centre increasing the interlayer separation dominates over the change to the in-plane conductivity due to the charge carrier density, the net effect would be a resistance increase. Such an interaction at the metal centre would be precluded for the analogous $\text{Ni}_3(\text{HITP})_2$ MOF as this is not a mixed valence compound, and Mirica et al.'s experiments found no evidence for redox communication between the ligand and metal centres.

4.5 Conclusion

In this chapter the responses of $\text{Cu}_3(\text{HHTP})_2$, $\text{Cu}_3(\text{HITP})_2$, $\text{Ni}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HITP})_2$ MOF sensors to NH_3 and NO_2 analyte gases are discussed. All four MOFs were made via solution synthesis methods and sensors were prepared using identical protocols and the sensing conditions were kept consistent throughout. Both the $\text{Cu}_3(\text{HHTP})_2$ and $\text{Cu}_3(\text{HITP})_2$ MOFs were found to respond with reversible resistance increases on exposure to NH_3 gas. By changing the solution synthesis components, samples of the same $\text{Cu}_3(\text{HHTP})_2$ MOF with different crystal morphologies were synthesised. Comparing the limits of detection of these sensors revealed that the morphology had a large impact on the sensing ability, with the flatter flake-like crystals giving a limit of detection to NH_3 of 0.12 ± 0.03 ppm compared to the 1.2 ± 0.2 ppm of the rod-like crystals. Manipulating the morphology of the MOF to improve sensing performance is a theme that will be built on in Chapter 8.

Three of the probed MOF sensors, $\text{Ni}_3(\text{HHTP})_2$, $\text{Cu}_3(\text{HHTP})_2$ and $\text{Cu}_3(\text{HITP})_2$ responded to NO_2 gas. For both of the HHTP-based MOFs this response came in the form of irreversible resistance increases, implying NO_2 -MOF interactions not specific to the metal are occurring. Contrastingly, the $\text{Cu}_3(\text{HITP})_2$ sensor responded to NO_2 by way of a reversible resistance increase. The response was rationalised in terms of redox communication between the metal centre and HITP ligand.

The work in this chapter also highlights limitations in the sensing behaviours. These include poor response magnitudes relative to baseline resistance drift and poor linearity in the relationship between sensing response and analyte concentration. The new MOF sensor fabrication methods introduced in the subsequent chapters will be assessed relative to these benchmarks as well as their effects on sensing figures of merit such as sensitivity and limit of detection.

Chapter 5

Synthesis of conductive metal-organic frameworks via metal nanocluster submersion

In this chapter I will present a new method of synthesising $\text{Cu}_3(\text{HITP})_2$ and $\text{Ni}_3(\text{HITP})_2$ MOFs from their constituent metal nanoclusters, in situ on a variety of substrates. I will first rationalise the demand for such an in situ method by discussing the relevant prior art, section 5.1, before detailing the final method and the experimental process through which the method was developed, sections 5.2 and 5.3. In section 5.4 I will show SEM images of the MOFs on the various substrates used, whilst in section 5.5 I will compare the rates of growth of the Ni and Cu MOFs on paper substrates. In section 5.6 I will discuss how the MOFs were characterised and in section 5.7 I will summarise the benefits of the presented method.

Much of the content of this chapter can be found in the paper titled ‘Conductive metal-organic framework synthesis from metal nanoparticle precursors’ by Abigail M. Lister, Yu Wang, Ben I. Armitage and Martin R. Castell, which has been submitted to IOP Journal of Physics: Materials.

5.1 Context

Drop-cast MOF systems often suffer from inhomogeneous distribution of MOF, poor conductivities due to high inter-particle contact resistance, and poor substrate adhesion. As such, alternatives to drop casting have been investigated. Better still are in situ synthesis routes that eliminate the need to deposit MOFs onto the desired substrates entirely. To realise the full

benefit of conductive MOFs in electronic devices or MOF-functionalised materials, current flow through the MOF itself must dominate over current flow through the substrate. For this to occur, the MOF needs to be adhered to an insulating surface. Methods such as the electrochemical growth of MOF are promising in terms of substrate adhesion, MOF homogeneity and morphological control. However, such methods reported thus far form the MOF on metal anodes,^{187,160,161} and so cannot be used as sensors without removal of the MOF from the metal and then re-adhering it to an insulating substrate.

In this chapter a method to synthesise two triphenylene-based MOFs, $\text{Cu}_3(\text{HITP})_2$ and $\text{Ni}_3(\text{HITP})_2$, in situ on glass, gold, paper and cotton substrates is presented. The method described involves direct synthesis of the MOFs from nanoclusters of the relevant metal. The nanoclusters are deposited on the desired substrate and the MOF is formed when the substrate is submerged in alkaline solutions of the desired ligand. The syntheses take place within one hour at room temperature and no harsh or expensive solvents are required. The MOF grows outwards from the deposited nanoclusters, and as such the resulting MOF coverage reflects the uniform distribution of the nanoclusters, thus eliminating issues such as the coffee-ring effect which are typical of drop-casting deposition methods. As the synthesis occurs directly from the metal, the advantages typical of salt-free synthetic methods are also retained – namely minimising the formation of unwanted by-products. We observe good adhesion of the MOF to the tested substrates and the mild solution conditions mean that we are confident that this method is scalable for use for MOF formation on the majority of substrates desired for applications in electronic devices or for MOF-functionalised materials.

5.2 Materials and methods

For the deposition of the Cu and Ni nanoclusters, an NL50 system manufactured by Nikalyte Ltd was used. The machine is a dc magnetron plasma sputtering source that operates at room temperature¹⁷¹ and deposits nanoclusters with depths measured in ng cm^{-2} (section 4.1.3). Four different substrates were used; Pt IDEs with 5 μm gap sizes on glass (Micrux Technologies, Spain), white card (WHSmith, UK), 200 thread count cotton percale (Dalston Mill Fabrics, UK) and Au (111) on mica (Georg Albert PVD, Germany). Deposition depths between 5000 and 8000 ng cm^{-2} were used depending on the substrate, as detailed in Figure 5.1. Each substrate was submerged in a vial containing a 2 mM solution of the HATP.6HCl organic starting material in a 4:1 water and ethanol solvent. To each vial, 375 μL of 19.4 M ammonia solution (Fisher Scientific UK), and 0.10 mmol of tributylmethylammonium methyl sulphate, TBMAMS, (Santa Cruz Biotechnology, USA) were added. Substrates were left in the ligand solutions for a set amount of time between one minute and 24 hours, after which they were removed from the solution and left to dry at room temperature in air overnight.

Substrate	Metal	Deposition amount / ng cm^{-2}
Au(111)	Cu	7000
Au(111)	Ni	7000
Cotton	Cu	8000
Cotton	Ni	8000
Paper	Cu	5000
Paper	Ni	5000
Glass/Pt interdigitated electrodes	Cu	7000
Glass/Pt interdigitated electrodes	Ni	7000

Figure 5.1: Table of the nanocluster deposition amounts in ng cm^{-2} per substrate per metal.

The scheme for the reaction is depicted in Figure 5.2 Justification for the inclusion of the TBMAMS electrolyte and alkaline environment will be discussed in section 5.3, and a proposed mechanism in light of the comparative growth rates of the different MOFs will be given in section 5.4.

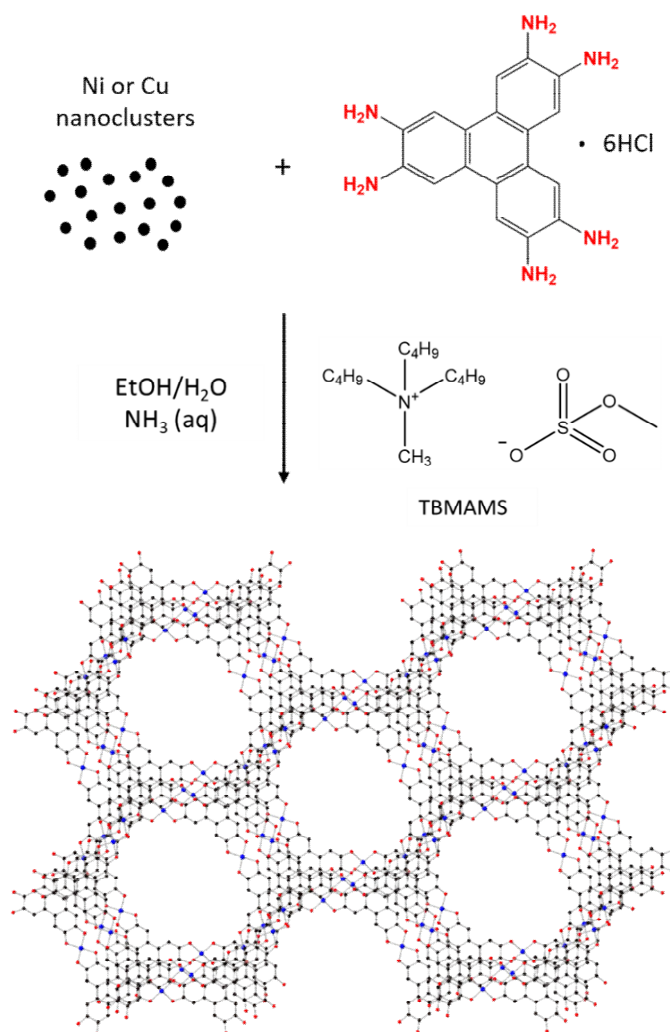


Figure 5.2: Reaction scheme for formation of the $\text{Cu}_3(\text{HITP})_2$ and $\text{Ni}_3(\text{HITP})_2$ MOFs from Ni or Cu nanoclusters. The metal nanoclusters react with the HITP·6HCl ligand (top right) in an ethanol/water solvent in the presence of TBMAMS electrolyte (centre right) and aqueous NH_3 . The products are hexagonal MOF sheets that stack with slipped parallel stacking to form 3D crystals with pore channels (bottom).

5.3 Method development

Numerous experiments were performed in which the amounts of ligand, electrolyte (TBMAMS) and ammonia solution were modulated. SEM and EDX were used to initially screen the samples made from different solutions to ascertain whether they were likely to have successfully made the desired MOFs. Syntheses attempted in the absence of electrolyte resulted in the formation of large (10 μm edge length) triangular crystals. Such crystals are visible in Figure 5.3 (left) which shows the result of leaving copper nanoclusters deposited on

paper in a solution of ligand and ammonia overnight in the absence of an electrolyte. EDX mapping of the highlighted region, Figure 5.3, shows that the large crystals are made up of carbon and nitrogen, with quantitative compositional analysis indicating that the crystal is 68.50 wt% carbon and 29.82 wt% nitrogen in addition to some oxygen, Figure 5.4. This is consistent with the weight percentages of carbon and oxygen in the HATP organic starting material. The absence of Cl in the EDX maps indicates that the crystals are crystalline forms of the HATP after removal of the coordinated HCl by the ammonia. In instances where high coverages of these crystals were observed, the amount of features containing both carbon and copper was low, suggesting that the formation of these crystals inhibits the formation of the desired MOF.

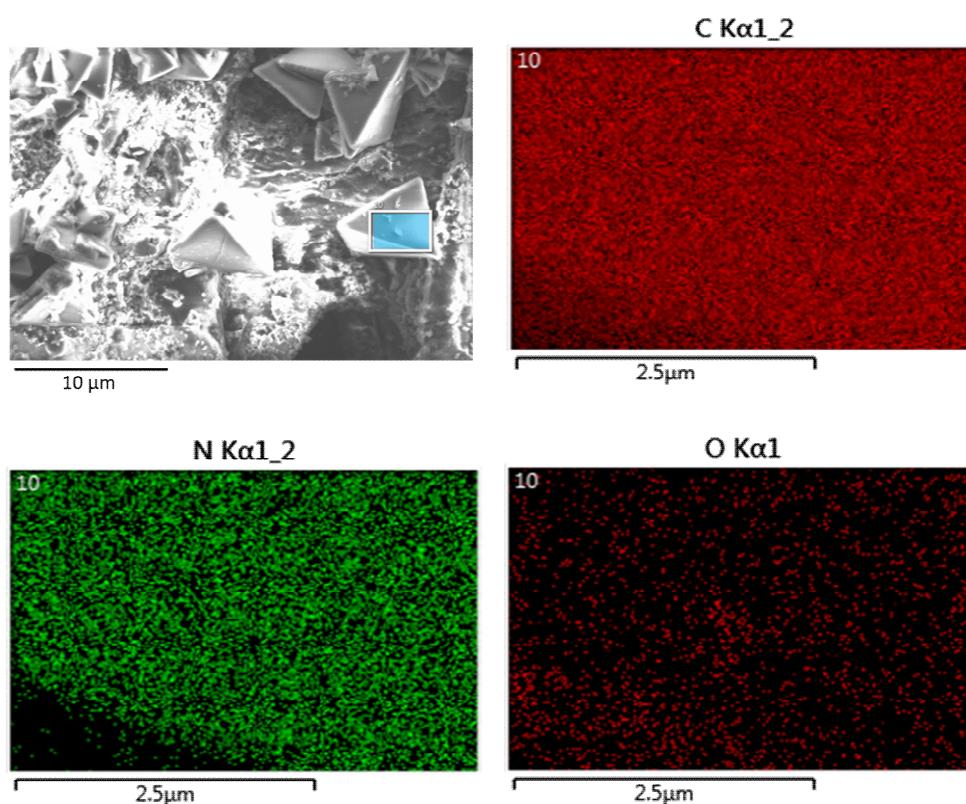


Figure 5.3: *Top left* – SEM image depicting the triangular prismatic crystals formed from submersion of copper nanocluster decorated paper in a HATP.6HCl and ammonia solution overnight. *Top right* – Carbon EDX map of the blue highlighted region. *Bottom left* – Nitrogen EDX map of the blue highlighted region. *Bottom right* – Oxygen EDX map of the blue highlighted region. The carbon and nitrogen maps show patterns of elements that reflect the shape of the prismatic crystal. The oxygen map contains less dense points, indicating that significantly less oxygen than carbon or nitrogen is present in this area.

Element	Line Type	Apparent Concentration	k Ratio	Wt%
C	K series	181.35	1.81345	68.50
N	K series	50.33	0.34765	29.82
O	K series	2.57	0.02248	1.68
Total:				100.00

Figure 5.4: Table of quantitative elemental composition data generated by the Aztec software used to perform EDX on the large prismatic crystal depicted in Figure 5.3 – top left. The weight percentages of carbon and nitrogen indicate that the carbon to nitrogen ratio in the crystal is the same as that in the HATP organic starting material.

By contrast, EDX mapping carried out on a copper-on-paper sample in an optimised solution of ammonia, HATP.6HCl and TBMAMS electrolyte produced the plots in Figure 5.5. The maps indicate that copper, carbon and nitrogen are present in the material grown on the surface of the paper, which is corroborated by the quantitative EDX output in Figure 5.6. The oxygen and calcium picked up by the quantitative analysis are components of the paper substrate. This implies formation of the desired $\text{Cu}_3(\text{HITP})_2$ MOF, but more rigorous characterisation can be found in section 5.6. Far fewer ligand crystals are observed under the SEM for samples made from electrolyte-containing solutions, confirming the key role that the TBMAMS plays in stabilising the HATP after the coordinated HCl is removed.

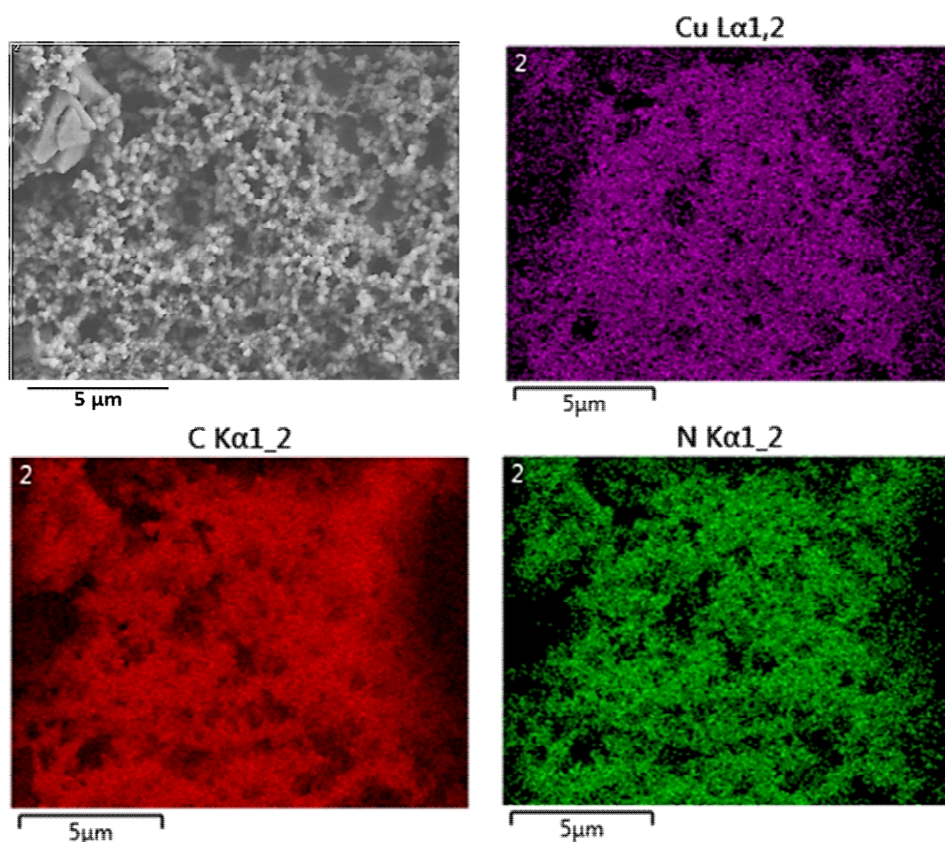


Figure 5.5: *Top left* – SEM image depicting the material grown from submersion of copper nanocluster decorated paper in an optimised solution of ligand, ammonia and electrolyte. *Top right* – Copper EDX map of the imaged area. *Bottom left* – Carbon EDX map of the blue imaged area. *Top right* – Nitrogen EDX map of the imaged area. The appearance of C, Cu and N atoms in the EDX maps coincide with the features depicted in the SEM image.

Element	Line Type	Apparent Concentration	k Ratio	Wt%
C	K series	96.39	0.96385	62.66
N	K series	15.70	0.10845	14.67
O	K series	12.31	0.10783	11.34
Ca	K series	4.92	0.04362	3.33
Cu	L series	8.56	0.08558	7.99
Total:				100.00

Figure 5.6: Table of quantitative elemental composition data generated by the Aztec software used to perform EDX analysis on copper-nanocluster decorated paper that has been submerged in an optimised solution of ligand, ammonia and electrolyte. Significant amounts of the copper, carbon and nitrogen MOF constituent elements are present. Oxygen and calcium are components of the paper substrates.

5.4 MOF growth

In order to determine the approximate time-scales over which the MOFs are growing on the substrates, time-point experiments were performed in which the different samples were left in the synthesis solutions for times varying between one minute and 24 hours. Paper samples with 5000 ng cm⁻² of metal nanoclusters deposited on them were used. For both the Cu and Ni HITP MOFs, darkening of the substrates with increased submersion time is visible by eye, as depicted by the optical images in Figure 5.7

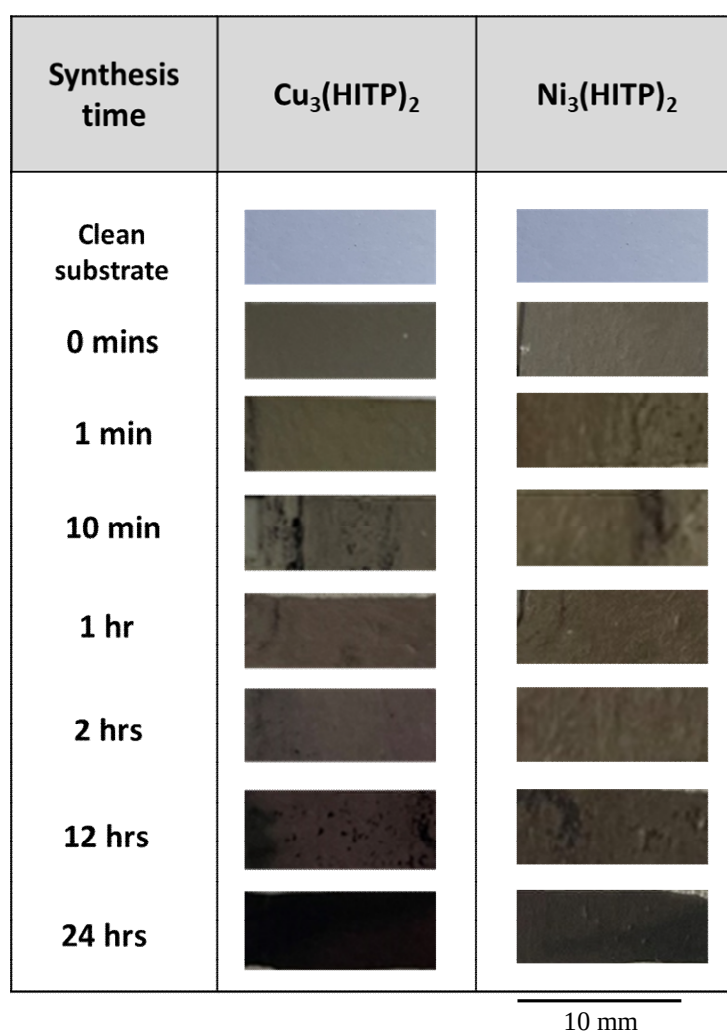


Figure 5.7 Photographs showing how the colours of nanocluster-decorated paper samples change with increasing MOF synthesis times for Cu₃(HITP)₂ MOF – **Left** and Ni₃(HITP)₂ MOF – **Right**. Both samples visibly darken as the nanoclusters are consumed to form the dark blue/black MOFs. The clean paper substrate before nanocluster deposition is depicted in the top row, whilst the nanocluster-decorated substrates before submersion in the MOF synthesis solution can be seen in row 2, labelled ‘0 mins’.

Closer inspection of the substrates was done via SEM. The resulting images of the $\text{Cu}_3(\text{HITP})_2$ MOF can be seen in Figure 5.8 and in Figure 5.9 for the $\text{Ni}_3(\text{HITP})_2$ MOF. By comparing the images taken before submersion in the synthesis solution (0 minutes) with those after 10 minutes of submersion in Figure 5.8, we can see that the $\text{Cu}_3(\text{HITP})_2$ MOF growth initiates from the nanoclusters within 10 minutes of submersion, with rounded features bigger than the original nanoclusters appearing on the surface of the paper fibres. Some bigger features on top of the surface are also visible after 10 minutes of submersion, with more appearing as the submersion time is increased. These are assumed to be formed from the amalgamation of smaller MOF crystallites. After 24 hours, the number of larger amalgamated crystallites is sufficient that there are multiple points where connected crystallites bridge the paper fibres.

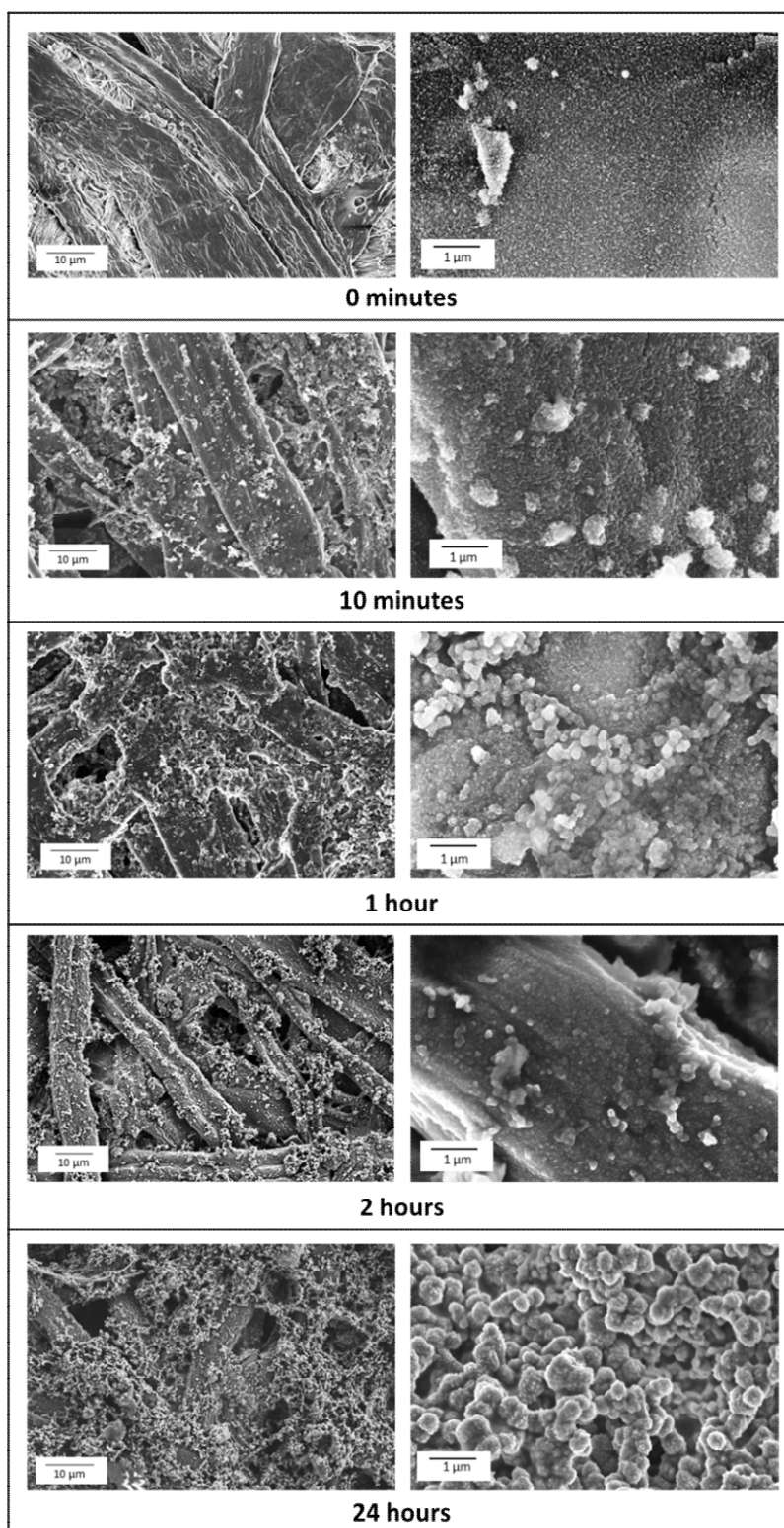


Figure 5.8 SEM images of copper nanoclusters deposited on paper after different submersion times in the MOF synthesis solution. The top row depicts only nanoclusters, whereas $\text{Cu}_3(\text{HITP})_2$ MOF is visible for the samples submerged in the ligand solution. Each row depicts the same sample imaged at different magnifications.

By submerging nickel nanoclusters on paper in identical ligand solutions for the same amounts of time, the morphologies and growth rates of the $\text{Ni}_3(\text{HITP})_2$ and $\text{Cu}_3(\text{HITP})_2$ MOFs can be compared. Whilst some broadening of the nanoclusters is visible between 0 minutes and 10 minutes, Figure 5.9, the changes are much more subtle than those observed for the $\text{Cu}_3(\text{HITP})_2$ MOF. No larger features formed from amalgamated crystallites are visible until two hours of submersion in the ligand solution. After 24 hours, the amalgamated crystallites have grown to approximately $0.5 - 0.8 \mu\text{m}$ in diameter, bigger than the average $0.3 \mu\text{m}$ $\text{Cu}_3(\text{HITP})_2$ MOF amalgamated crystallites formed after the same amount of time. A greater proportion of the $\text{Ni}_3(\text{HITP})_2$ crystallites however are adhered to the surface as opposed to between the fibres, in that less bridging of the fibres is observed for the $\text{Ni}_3(\text{HITP})_2$ 24 hour sample than in the analogous $\text{Cu}_3(\text{HITP})_2$ sample. Also of note are the contrasting shapes of MOF crystals, with the $\text{Cu}_3(\text{HITP})_2$ crystals more rounded and the $\text{Ni}_3(\text{HITP})_2$ crystals growing as fine shards that then form rounded features on amalgamation. In the case of both MOFs, these shapes are consistent with those synthesised from different methods reported in literature.^{139,188}

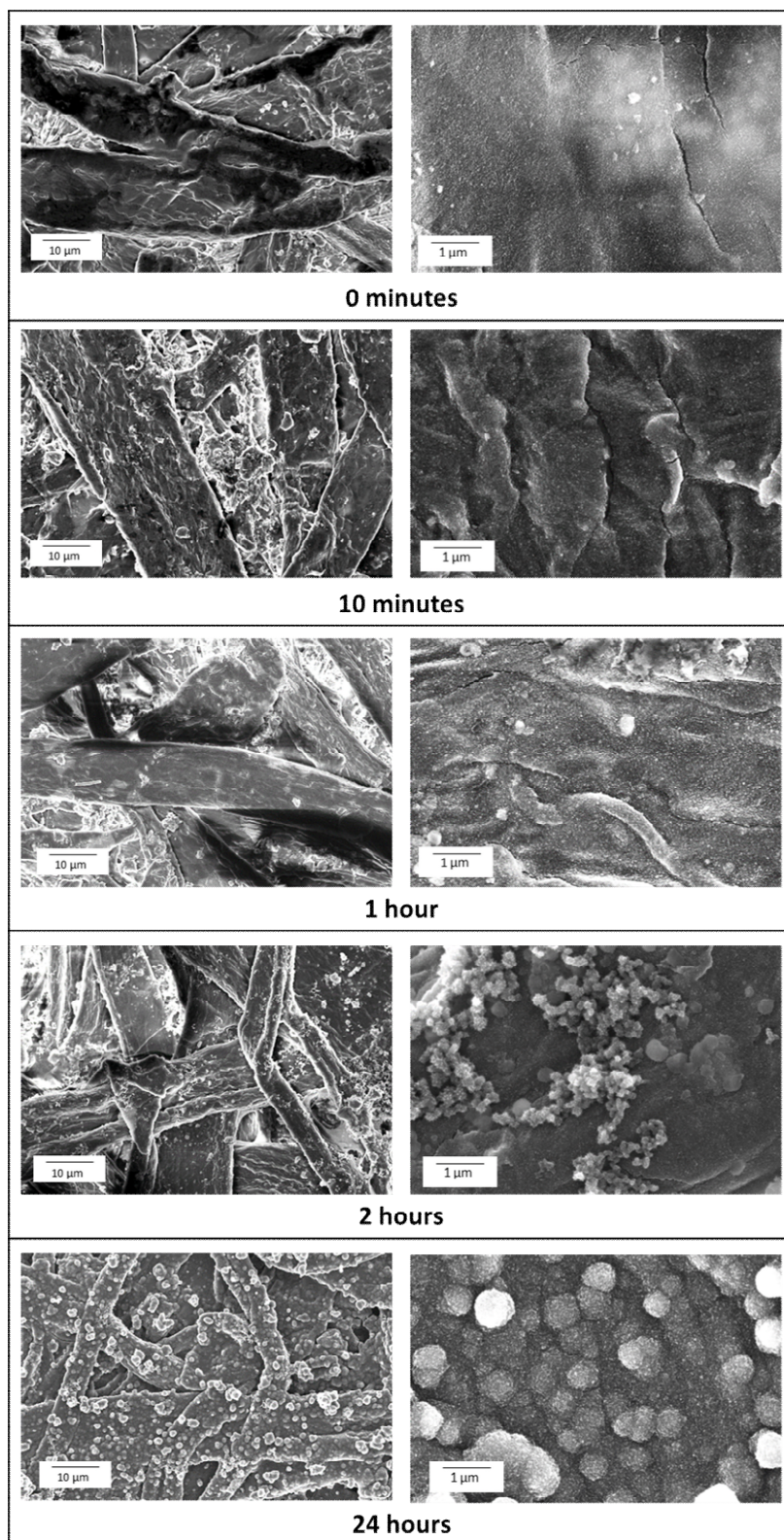
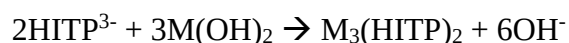
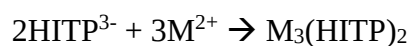
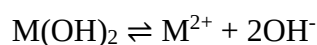


Figure 5.9: SEM images of copper nanoclusters deposited on paper after different submersion times in the MOF synthesis solution. The top row depicts only nanoclusters, whereas $\text{Ni}_3(\text{HITP})_2$ MOF is visible for the samples submerged in the ligand solution. Each row depicts the same sample imaged at different magnifications.

Despite Ni metal being more reactive than Cu, the SEM images in Figures 5.8 and 5.9 indicate that growth of the $\text{Ni}_3(\text{HITP})_2$ MOF proceeds slower than that of the $\text{Cu}_3(\text{HITP})_2$. Potential reasons for this can be ascertained by considering the mechanism of MOF formation. The reaction is suspected to proceed via formation of small amounts of metal hydroxide at the surfaces of the nanoparticles, initiated by the alkaline environment. In parallel, the hydroxide ions in solution will deprotonate one of the two amine groups on each arm of the HATP molecules to form the partial imine form. Subsequent oxidation of this molecule by dissolved oxygen in the solution results in a partial imine radical which is then deprotonated to form the activated HITP^{3-} species that can form the MOF. The growth of the MOF can occur at two main locations: the interface between the metal hydroxide on the surface of the nanoparticles (interface growth), or on the surface of the MOF (surface growth). For interface growth the activated ligands diffuse through the MOF to the nanoparticle surface and react with the surface metal hydroxide:



Alternatively, surface growth can involve the dissolution of the metal hydroxide to release M^{2+} ions around the nanoclusters, which then diffuse through the MOF. Once the M^{2+} ions reach the surface of the MOF they react with the activated HITP to perpetuate growth:



For both growth modes the metal in the nanoparticles is consumed as the MOF grows. The MOF is anchored to the nanoparticles acting as the metal source, which in turn are anchored to the substrate on which they were deposited. The faster growth rate of $\text{Cu}_3(\text{HITP})_2$ compared to $\text{Ni}_3(\text{HITP})_2$ may be due to the higher solubility of $\text{Cu}(\text{OH})_2$ (39.8 g L^{-1}) versus $\text{Ni}(\text{OH})_2$ (0.13 g L^{-1}) in water at 20°C .

The TBMAMS electrolyte was added to increase the concentration of counter ions that can react with any excess ammonia. This prevents the ammonia reacting with the HCl coordinating to the HATP organic starting material, the removal of which causes the HATP to rapidly crystallise out of the solution. Ammonia is necessary in the solution to facilitate the formation of the metal hydroxide reaction intermediates, but the nature of the nanocluster deposition makes it non-trivial to determine the number of moles of metal present accurately. Exact molar ratios of the metal and alkali can therefore not readily be calculated, but by adding the electrolyte, we can always use an excess of ammonia solution whilst also preventing crystallisation of the ligand.

5.5 Substrate investigations

By following the optimised experimental procedure outlined in section 5.2, MOF growth was attempted from nanoclusters deposited on Pt/glass IDEs, white card, cotton and Au (111) on mica. Submersion of the nanoclusters on various substrates in the ligand solution for 1 hour resulted in noticeable colour changes by eye and changes in the surface texture observable via SEM. In Figure 5.10, the SEM images resulting from submerging copper nanocluster-decorated substrates in the ligand solution for 1 hour are shown. An underlying surface texture of rounded features bigger in size than the original nanoclusters is observed for all of the substrates. This supports the idea that the MOF grows outwards from the nanoclusters. In addition to the change in underlying texture, some bigger features sitting on top of the surface are visible, appearing mostly in white in the SEM images. These are assumed to be amalgamated crystallites of the MOF.

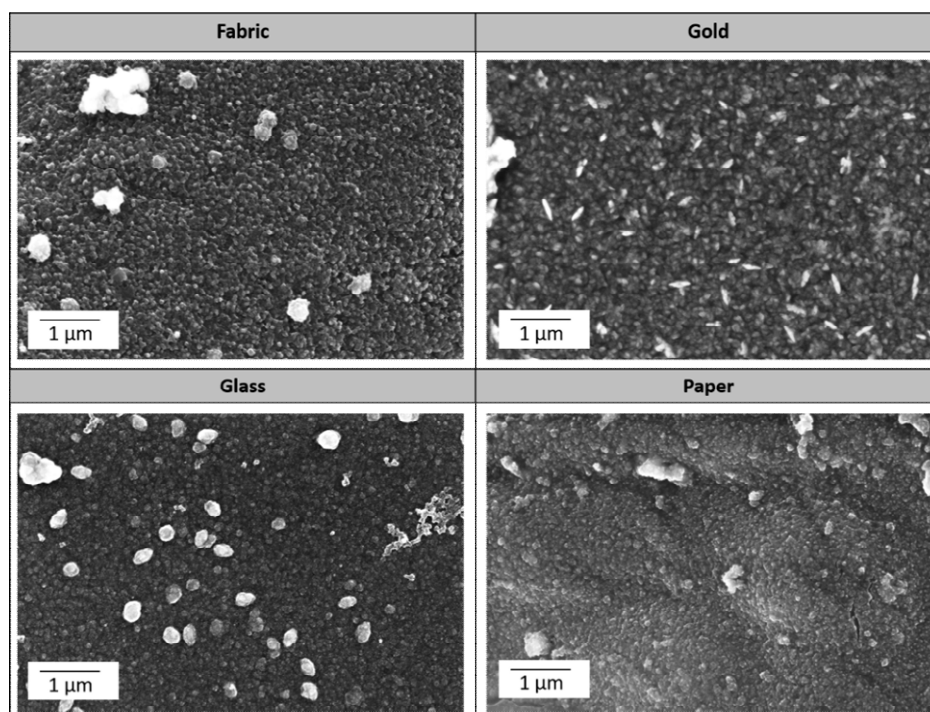


Figure 5.10: SEM images showing the surface morphology of $\text{Cu}_3(\text{HITP})_2$ MOF on fabric, gold, glass and paper substrates formed from deposition of copper nanoclusters onto the substrates and subsequent submersion in a solution of the HATP organic starting material for one hour.

When nickel nanocluster-decorated Pt/glass IDEs, paper, gold and fabric substrates were submerged in identical HATP solutions for one hour, as the copper samples above, the SEM images in Figure 5.11 were obtained. As per the copper samples, an underlying surface texture of rounded features bigger in size than the original nanoclusters is observed for all of the substrates. The underlying features however, are noticeably smaller for the nickel samples than the analogous copper samples. This is consistent with the slower rate of formation of the $\text{Ni}_3(\text{HITP})_2$ MOF as rationalised in section 5.4. Across the glass, gold and paper samples, there are fewer larger features that can be attributed to amalgamated crystallites than in the copper samples. This is also as expected when considering the relative rates of reactions of the copper and nickel MOFs. The fabric sample however, shows a surprisingly high concentration of amalgamated crystallites in the imaged region. This is likely due to the fibrous and rough nature of the substrate, whereby nanoclusters deposited in between fibres or on the sides of the fibres will be adhered less strongly to the substrate and so form MOF crystallites that can more easily detach and amalgamate.

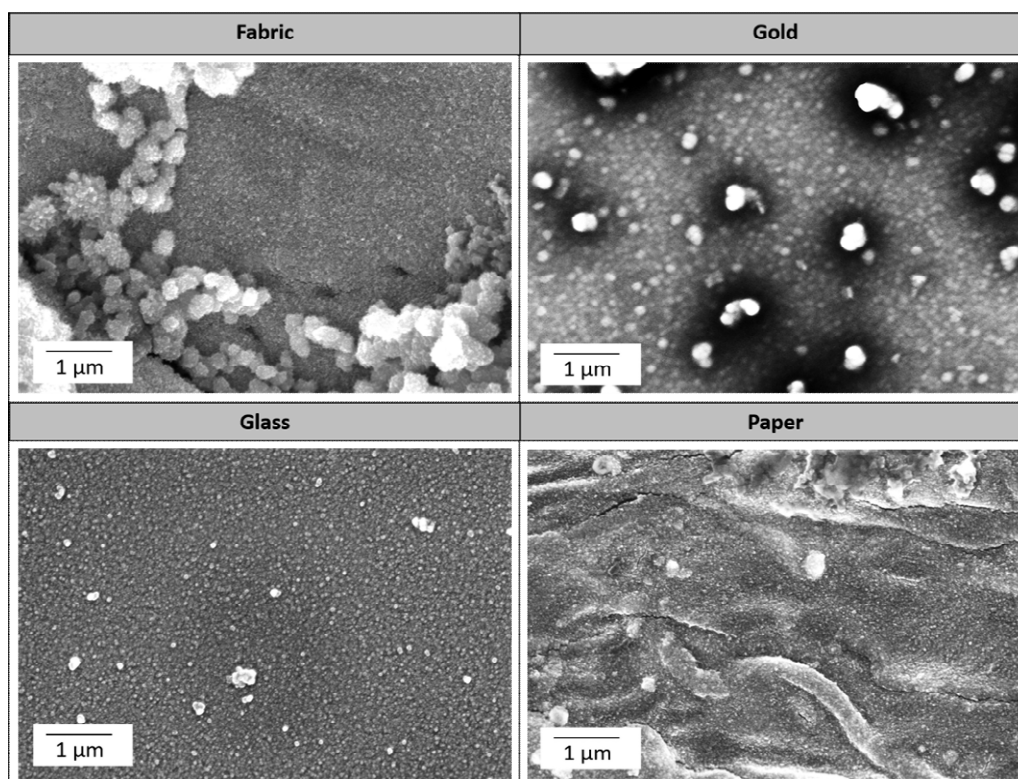


Figure 5.11: SEM images showing the surface morphology of $\text{Ni}_3(\text{HITP})_2$ MOF on fabric, gold, glass and paper substrates formed from deposition of Ni nanoclusters onto the substrates and subsequent submersion in a solution of the HATP organic starting material for one hour.

5.6 Characterisation

Sample characterisation is important for the work detailed in this chapter to prove that the new method introduced can reliably generate the desired MOFs. As the method uses nanoparticles covering small areas of substrate as the metal source for the MOF, the MOFs are synthesised in small amounts. Moreover, most of the MOF forms strongly adhered to the substrates. XPS, section 5.6.1 could be performed with the MOFs in situ on the glass IDE substrates on which they were formed. However, for PXRD and TEM, loose MOF powder samples were required. Sufficient MOF powder could be obtained for TEM by scraping material off the paper substrates, but not enough MOF could be obtained for PXRD with this method. Alternative arrangements as described in section 5.6.3 were therefore made.

5.6.1 X-ray photoelectron spectroscopy

XPS was carried out on a K-alpha machine from Thermo Scientific, USA. The MOF-on-IDE samples were analysed without any further processing. An electron neutraliser was used to prevent charge build up. The XPS survey scans depicted in Figure 5.12 illustrate the presence of the elements present in the MOF and are consistent with previously reported XPS spectra for both MOFs.^{188,189}

The survey scan for the Cu-HITP MOF in Figure 5.12 – left shows peaks corresponding to the binding energies of the expected elements. The main peaks at 285.0 eV (C 1s), 399.0 eV (N 1s), and 934.1 eV (Cu 2p) are labelled in bold. The less sharp peaks at 571.0, 651.0 and 716.7 eV are copper Auger peaks. Also labelled is an intense O 1s peak at 532.0 eV, but this can be attributed to the oxygen present in the substrate due to a similarly intense peak being visible in the spectrum of the clean IDE. The smaller peaks visible at 76.7 and 123.4 eV can be assigned to photoelectrons from the Cu 3p and Cu 3s respectively. The minor peaks at 169.0 and 199.0 eV can be assigned to S and Cl 2p sub-shells. These peaks do not appear in the survey scan of the clean electrode, and therefore indicate the presence of some impurities. S is present in the TBMAMS electrolyte used and Cl in the HCl coordinated to the HITP organic starting material. Quantitative analysis by the XPS software however indicates that the atomic % of Cl is 0.59 % and that of S is 0.94 %. The peaks at 103.0 and 153.6 eV can be assigned to Si 2p and Si 2s sub-shells, which are also present in the survey scan of the clean IDE.

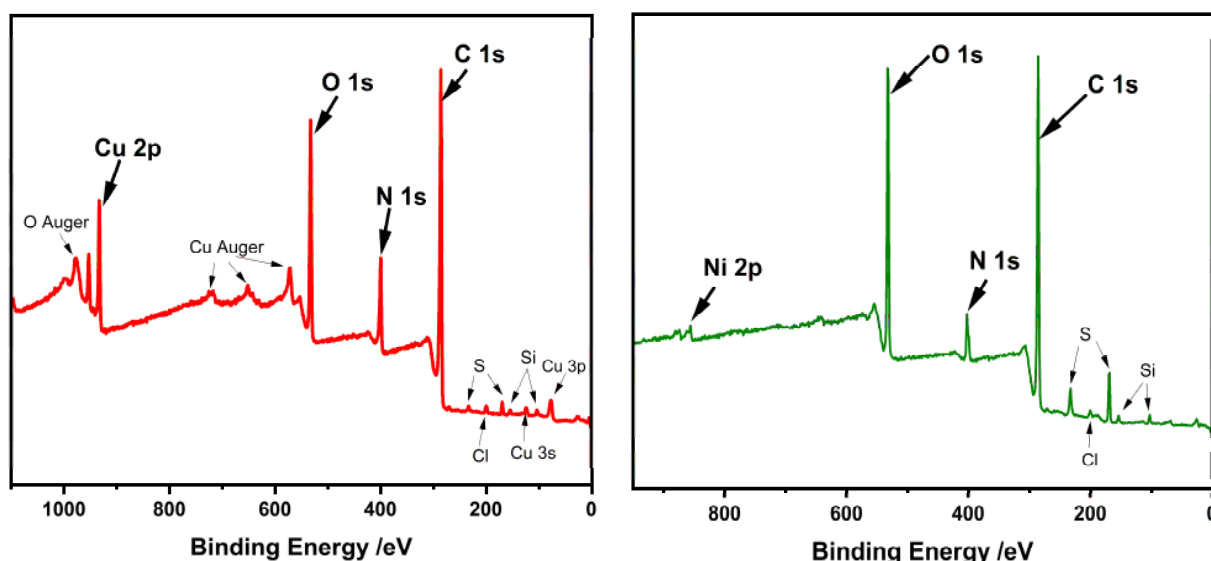


Figure 5.12: *Left* - XPS survey scan for the $\text{Cu}_3(\text{HITP})_2$ MOF on glass interdigitated electrode substrate. *Right* - XPS survey scan for the $\text{Ni}_3(\text{HITP})_2$ MOF on glass interdigitated electrode substrate. Labelled in bold are peaks corresponding to the elements in the respective MOFs. Cl peaks arise from the HATP.6HCl starting material. Si is present in the electrode substrate. The S peak indicates contamination with a sulphur-containing species.

The survey scan depicted in Figure 5.12 - right is that of the $\text{Ni}_3(\text{HITP})_2$ MOF synthesised in situ on the glass interdigitated electrode. Again the peaks at 25.0, 102.0, 153.0 and 532.1 eV can be assigned to components of the IDE substrate. As in the case of the $\text{Cu}_3(\text{HITP})_2$ MOF, there is some evidence of contamination by Cl and S, with the peak at 232.1 eV indicative of S presence, and that at 199.9 eV indicative of Cl presence. The Ni 2p peak appears at a binding energy of 855.7 eV, whilst the C 1s appears at 285.3 eV and the N 1s at 402.0 eV. Evidence that a chemical reaction has taken place can be found by looking at the component peaks of the N 1s and C 1s features, but the most compelling evidence is seen by analysing narrow area scans centred at the metal 2p binding energies, Figures 5.13 and 5.14.

By inspecting Figure 5.13, the copper $2p_{3/2}$ and $2p_{1/2}$ peaks can be identified at 932.6 eV and 952.4 eV respectively. These binding energy values are consistent with those expected for copper in its +1 oxidation state or metallic copper. Two satellite peaks at higher binding energies accompany each of the peaks. By comparing XPS spectra with those of copper and

its' known compounds from the ThermoFisher Elemental Database, it can be noted that satellite peaks are only observed when the copper is present in its oxidised state. Both the $2p_{3/2}$ and $2p_{1/2}$ satellite peaks are observed for substances containing Cu^{2+} , and only the $2p_{1/2}$ satellite is visible when Cu^+ is present. The presence of the satellite peaks in the spectrum in 5.13 therefore provides evidence that the copper nanoclusters have been oxidised, likely during formation of the $\text{Cu}_3(\text{HITP})_2$ MOF. It is suspected that the copper in the MOF is present as a mixture of Cu^+ and Cu^{2+} .^{143,190} There is no obvious peak splitting for the $2p_{3/2}$ and $2p_{1/2}$ peaks but the peaks are noticeably asymmetrical, with slight shoulders of the peaks visible on the higher binding energy side, suggesting the presence of Cu^{2+} in addition to Cu^+ . As the binding energies for metallic Cu and Cu^+ are coincident for copper compounds, it cannot be ruled out that residual copper cores remain on the substrate. The satellite peaks however make us sure that some oxidised Cu is present.

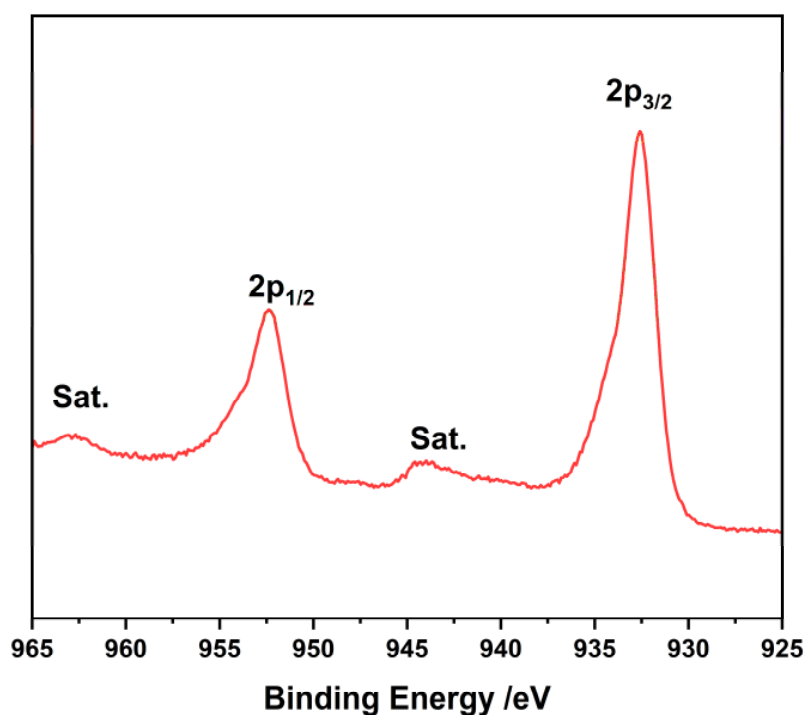


Figure 5.13: Narrow area XPS scan of the Cu 2p region for a $\text{Cu}_3(\text{HITP})_2$ sample synthesised from Cu nanoclusters on a glass IDE substrate. The Cu $2p_{1/2}$ and $2p_{3/2}$ peaks are visible. The presence of satellite peaks indicates that some Cu is present in an oxidised state. The asymmetry in the main peaks suggests that both Cu^+ and Cu^{2+} ions are present.

Similarly, by inspecting Figure 5.14, the nickel $2p_{3/2}$ and $2p_{1/2}$ peaks can be identified at 855.7 eV and 873.2 eV respectively. Satellite peaks can be observed at slightly lower binding energies for each of the $2p$ peaks. However, by consulting database XPS data, it can be seen that satellite peaks appear for both elemental nickel and oxidised nickel. The presence of satellite peaks can therefore not be used as evidence that the nickel nanoclusters have undergone a chemical reaction. Instead, evidence can be found by comparing the binding energies recorded for the MOF sample with those for the pure metal. It is well reported that the $2p_{3/2}$ electrons in elemental nickel have a binding energy of 852.6 eV, whilst compounds containing oxidised nickel have higher binding energies up to 856.1 eV.¹⁹¹ This means that the Ni $2p_{3/2}$ peak at 855.7 eV recorded for the $\text{Ni}_3(\text{HITP})_2$ sample discussed here contains Ni in an oxidised state, suspected to be part of the $\text{Ni}_3(\text{HITP})_2$ MOF. The absence of peaks at lower binding energies consistent with metallic Ni, suggests that the Ni on the electrodes has been fully converted to its oxidised species.

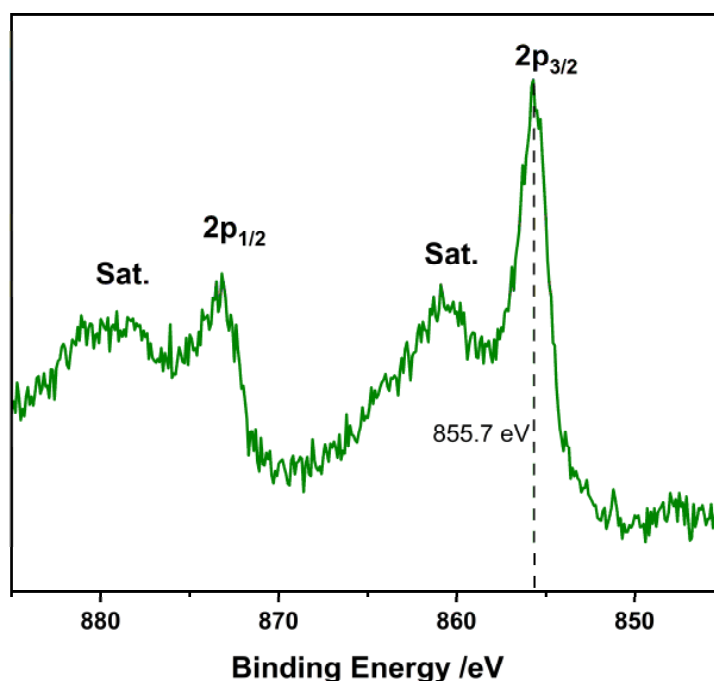


Figure 5.14: Narrow area XPS scan of the Ni $2p$ region for a $\text{Ni}_3(\text{HITP})_2$ sample synthesised from Ni nanoclusters on glass IDEs. Ni $2p_{1/2}$ and $2p_{3/2}$ peaks are visible as are their associated satellite peaks. The values of the main peak binding energies are consistent with Ni being present in its oxidised state.

5.6.2 Powder X-ray diffraction

The thickness of the MOF layers relative to the substrates' roughness meant that PXRD experiments could not be carried out with the MOF on the substrates using the available equipment. Thin film PXRD attempted with an Empyrean Panalytical XRD machine was not successful in probing the MOF, with only peaks for the substrates observed. Attempts were made to scrape MOF off the substrate in order to obtain bulk powder suitable for conventional PXRD experiments. Both MOFs were however very strongly adhered to the substrates, with vigorous sonication removing very little MOF from the surface. Scraping the surfaces with a spatula only served to remove parts of the substrate as well. In the case of the $\text{Cu}_3(\text{HITP})_2$ MOF, the synthesis was therefore scaled up using copper foil instead of nanoparticles for the purposes of PXRD. Enough MOF was produced in this experiment that the powder could be scraped off the foil and the plot in Figure 5.15 was obtained with a Rigaku Miniflex machine (1.54 Å $\text{CuK}\alpha$ X-ray source). Peaks were observed at $2\theta = 4.7^\circ, 9.6^\circ, 12.6^\circ, 16.6^\circ$ and 27.4° which are consistent with the peak positions reported in literature.¹⁶³ When indexed according to a hexagonal unit cell, these peaks correspond to lattice parameters of $a = b = 21.7\text{\AA}$ and $c = 3.2\text{\AA}$. The (001) peak at $2\theta = 27.5^\circ$ is however significantly sharper than typically reported, suggesting enhanced long range order in the c -direction for MOFs synthesised via this method. The two additional peaks at $2\theta = 35.6^\circ$ and 38.6° can be assigned to CuO crystals. The CuO is expected to form from the $\text{Cu}(\text{OH})_2$ intermediate as the foil dries after removal from solution. We would anticipate less CuO to be produced for the MOF formed from the nanoclusters due to the excess of ligand as opposed to metal. Unfortunately not enough material could be produced to obtain PXRD data for the $\text{Ni}_3(\text{HITP})_2$ MOF, even after substituting Ni nanoclusters for Ni mesh. There was enough material however for TEM to be carried out.

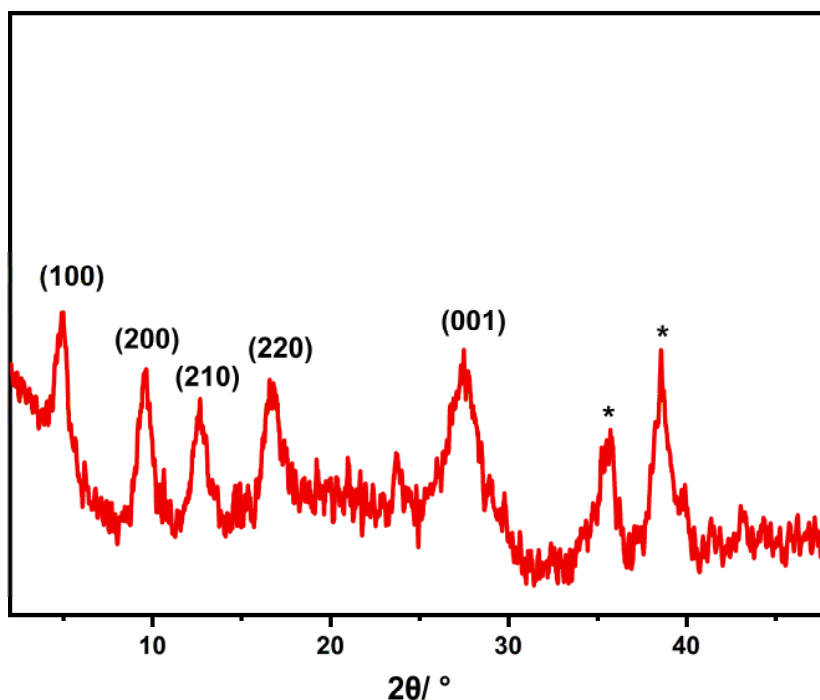


Figure 5.15: Powder X-ray diffraction pattern for $\text{Cu}_3(\text{HITP})_2$ synthesised from copper foil. Visible peaks can be indexed to (100), (200), (210), (220) and (001) reflections in the MOF. The peaks marked with asterisks indicate that CuO crystals are also present.

5.6.3 Transmission electron microscopy

Material scraped off the surface of the substrates was sonicated in ethanol and deposited on Cu TEM grids. Transmission electron microscopy, TEM, was then carried out on a JEM-2100 machine (JEOL Ltd, Japan) in order to probe the lattice structure of the MOFs. In both cases, stacks of the 2D MOF sheets were visible and the interlayer spacing could be measured. This was done using ImageJ by measuring the distance between 10 parallel lines depicting layers of MOF, then taking the average by dividing this value by 10. Representative interlayer distances are marked in white in Figure 5.16. For the Ni MOF, Figure 5.16 – left, the interlayer spacing was measured to be 3.3 Å. For the Cu MOF, Figure 5.16 - right, the spacing was measured to be 3.2 Å, which is consistent with the value for lattice parameter c ascertained from the PXRD results. The larger hexagonal pores with approximate diameter of 2 nm were more difficult to find because of the thickness of the crystallites. When they were observed,

the regions were destroyed by the electron beam before clear images could be obtained. The values of the interlayer spacing obtained in these experiments is consistent with those reported in literature for both MOFs.^{139,192}

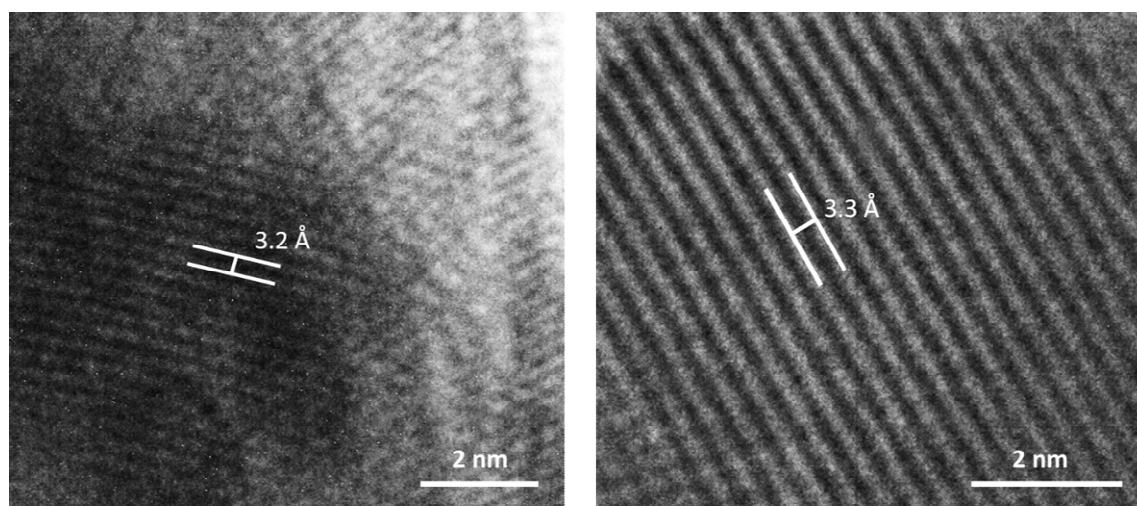


Figure 5.16: *Left - TEM image depicting the 3.3 Å interlayer spacing in $\text{Ni}_3(\text{HITP})_2$ MOF. Right - TEM image depicting the 3.2 Å interlayer spacing in $\text{Cu}_3(\text{HITP})_2$ MOF. Spacings were measured using ImageJ and the calculated averages are represented in white on each image.*

5.7 Conclusion

A method to synthesise $\text{Cu}_3(\text{HITP})_2$ and $\text{Ni}_3(\text{HITP})_2$ MOFs in situ on a variety of conductive and insulating substrates has been presented. The method uses metal nanoclusters as the metal source to synthesise the MOFs via submersion of the decorated substrates in an alkaline solution of the ligand in the presence of an electrolyte. SEM imaging revealed that the MOFs begin to form on the substrate within 10 minutes of submersion in the ligand solution. Through using metal nanoclusters deposited with a magnetron sputtering machine as the metal source, any substrate that fits inside the sputtering chamber can be used. As such, this method is expected to be widely applicable to substrates beyond the cotton, glass, paper and gold explored in this work. This method combines the potential for use on many substrates with

being salt-free, rapid, and not requiring toxic solvents or elevated temperatures. The proven effectiveness of the method presented in synthesising conductive MOFs in situ on interdigitated electrodes could be employed in the area of chemiresistive sensing, whilst the mild conditions in general make this method promising for direct growth on delicate electronics.

Chapter 6

Electrochemical growth of $\text{Cu}_3(\text{HHTP})_2$ from copper nanoclusters for chemiresistive gas sensing

In this chapter I will describe a new route to synthesise $\text{Cu}_3(\text{HHTP})_2$ conductive MOF via electrochemical synthesis from copper nanoclusters, producing the MOF in situ on the electrodes required for gas sensing. It should be noted that the $\text{Cu}_3(\text{HITP})_2$ and $\text{Ni}_3(\text{HITP})_2$ MOFs discussed in chapter 5 do not require an applied electrical potential to form so the method described in chapter 5 can be used instead of the one outlined in this chapter. On the other hand, the $\text{Cu}_3(\text{HHTP})_2$ MOF synthesised in this chapter cannot be made via the nanocluster submersion method detailed in chapter 5.

In section 6.1 I will highlight the limitations of previously reported synthesis methods for this MOF and how the method presented herein seeks to address these. In section 6.2 I will describe how the presented method should work in theory, followed by a description of how the experimental conditions were optimised followed by the final experimental procedure used. In section 6.3 I will use SEM images to describe how the MOF grows from the nanoclusters, whilst in section 6.4 I will present XPS, Raman and PXRD evidence that the method is successful in generating the desired MOF. In section 6.5 the sensing performance of sensors made through this method will be investigated.

Much of the content of this chapter can be found in the paper titled, ‘Electrochemically grown $\text{Cu}_3(\text{HHTP})_2$ metal-organic framework from copper nanoclusters for chemiresistive gas sensing’ by Abigail M. Lister, Ben I. Armitage, Yu Wang, Runze Chen, Weishuo Li and Martin R. Castell. It has been submitted for review by ACS Applied Nanomaterials.

6.1 Context

To maximise the advantages of MOFs as chemiresistive sensing media, efficient and reliable methods of integrating the MOFs into the sensors are required. Obtaining a uniform dispersion of MOF on an insulating substrate is desirable for chemiresistive sensing applications. Methods to synthesise the MOF in situ on the desired substrates have been investigated to circumvent the need for drop-casting. Such methods include liquid-phase layer-by-layer epitaxial self-assembly,¹⁴⁸ vapour-assisted conversion¹⁵⁴ and spin-coating.¹⁹³ Whilst the above in situ methods result in more uniformly distributed MOF on the substrate, they do not address the issue whereby the measured resistance across the electrodes is likely to be dominated by the contact resistance between the particles. Methods to electrochemically grow the MOF have been explored as routes to reduce the effects of contact resistance in the sensors.^{194,160} However, the methods published so far result in the MOFs synthesised attached to conductive substrates. They therefore cannot be used as chemiresistive sensors because the current would simply flow through the remaining copper anode as opposed to the less conductive MOF on the surface. Steps must therefore be taken to remove the MOF from the conductive substrate and re-adhere it to an insulating one.

In this chapter a route to electrochemically synthesise $\text{Cu}_3(\text{HHTP})_2$ from copper nanoclusters in situ on the insulating glass substrates required for sensing is presented. The method requires no assistance from oxygen bubbling and no removal of the MOF from the substrate in order for it to be used as an NH_3 sensor. A potential is applied to oxidise the metal nanoclusters and initiate MOF growth. This ensures that all the MOF that grows is electrically connected to the electrodes that the potential will be applied across when operated as a chemiresistive sensor. Some of the high contact resistance MOF-MOF grain boundaries are replaced by copper-MOF boundaries whilst still ensuring current must flow through the MOF rather than only bulk metal. Growing the MOF from nanoclusters enables control over the regions where the MOF

forms through patterning at the nanocluster deposition stage. Uniform distribution of MOF is ensured and the coverage of MOF can be easily controlled by changing the synthesis time.

6.2 Methodology

This section will start with a diagrammatic discussion of the principles behind the method developed in this chapter. This is followed by the final experimental protocol used.

6.2.1 Method in theory

The aim of the synthesis method described here is to improve chemiresistive sensing performance by ensuring that all the electrically conducting pathways are connected to the electrodes. This aim is necessarily achieved by electrochemical growth because MOF growth will only occur if there is a potential, and this potential originates from one of the electrodes. The approach described here starts by depositing copper nanoclusters onto clean IDEs using a magnetron discharge source (section 3.1.3). Just enough nanoclusters are deposited to take the IDEs from insulating to having a resistance between 20 and 40 k Ω across them, as measured according to Figure 6.1 (a). The MOF growth process is illustrated schematically in Figure 6.1 where in (b) just enough copper nanoclusters (orange) have been deposited to generate some conductive pathways across the insulating gaps, depicted by black lines. The copper nanocluster-decorated IDE is then used to grow the Cu₃(HHTP)₂ MOF. This occurs via submersion in a solution of the HHTP organic starting material and electrolyte, whilst a positive potential is applied to both sides of the IDE to oxidise the Cu. This results in the MOF, depicted in green in Figure 6.1 (c), growing outwards from the copper nanoclusters that are experiencing a positive potential due to their electrical connection to the electrodes. This

is accompanied by a decrease in size of the nanoclusters as the copper is consumed to form the MOF. The result is an increase in the number of conductive pathways bridging the electrodes, all of which require current to flow through the MOF. This MOF decorated electrode is then a ready-to-use chemiresistive sensor.

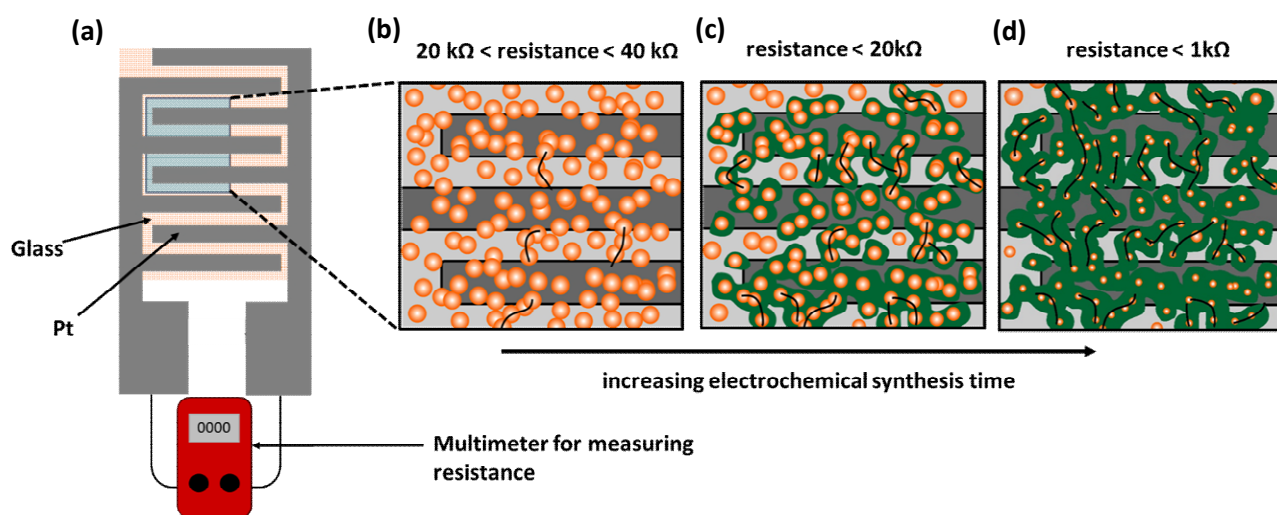


Figure 6.1: (a) Schematic representation of a Pt on glass interdigitated electrode with copper nanoclusters deposited on it. (b) Portion of an IDE on which copper nanoclusters (orange) have been deposited before any electrochemical synthesis. Limited conductive pathways (black lines) exist between the electrodes. (c) After electrochemical synthesis has commenced, MOF (green) has grown outwards from the copper nanoclusters resulting in more conductive pathways bridging the electrodes. (d) As the electrochemical synthesis continues more MOF and more conductive pathways bridging the insulating gaps arise. This results in a reduced electrical resistance across the IDE.

Copper nanoclusters were deposited onto IDEs with Pt fingers separated by insulating glass gaps, as is illustrated schematically in Figure 6.1 (a). Before deposition of any conductive materials to bridge the insulating gaps, inserting a multimeter between the contact pads will give an infinite resistance reading. The measured resistance decreases as the MOF electrochemically grows.

The potential applied to the nanocluster-decorated electrode to trigger copper oxidation and initiate MOF formation was +0.435 V. This potential was chosen in light of the results of Bradshaw et al.'s investigations into the electrochemical growth of the same MOF from bulk

Cu electrodes.¹⁶⁰ They performed a series of electrochemical experiments in which different potentials between 0.435 V and 0.7 V were applied. They found that the sharpest PXRD peaks and largest MOF crystals were present for the sample synthesised at +0.435 V, which they attributed to the slower oxidation rate meaning that there was sufficient time for ligands to coordinate to the Cu ions. They also found that the (001) peak in the PXRD spectrum became less sharp as the synthesis potential was increased, indicating that there was less long range order in the crystals. Since the π - π interlayer stacking is suspected to be a significant contributor to the conductivity, it was considered best to select the lower potential for synthesis to maximise the through-space charge transport in the *c*-direction.¹⁶⁰ If the potential was decreased below +0.435 V, there would be a risk of the potential not being high enough for the Cu oxidation to occur. A potential of +0.435 V was therefore selected as the optimum potential for this experiment.

6.2.2 Experimental protocol

Copper nanoclusters were deposited onto Pt inter-digitated electrodes, IDEs, with 5 μm gap sizes on glass (Micrux Technologies, Spain). An NL50 system manufactured by Nikalyte Ltd was used to deposit the copper nanoclusters onto the IDEs. 7000 ng cm^{-2} of copper nanoclusters with diameters between 10 and 50 nm were deposited. This resulted in IDEs with resistances between 100 and 300 $\text{k}\Omega$. Each IDE was annealed for 2 hours on a hot plate at 200 $^{\circ}\text{C}$ to reduce the resistance to between 20 and 40 $\text{k}\Omega$. The aim of this was to improve adhesion of the nanoclusters to the glass of the IDE and improve conductivity by initiating necking between the particles, thereby increasing the proportion of nanoclusters to which the potential for MOF formation is applied.

A 2.6 mM of 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and 0.021 M solution of methyltetrabutylammonium methyl sulphate (TBMAMS) electrolyte was made up in a 4:1 ethanol and deionised water mixture. The solution was degassed by bubbling N₂ gas through the solution for 10 minutes before the potential was applied. A standard 3-electrode set-up as described in section 3.1.4 was used. The two sides of the copper nanocluster-decorated IDE were connected together and a potential of +0.435 V was applied to grow the MOF. The potential was applied for times between one minute and 4 hours for each electrode. A morphological comparison of the MOF formed after different electrochemical synthesis times will be given in the following section.

6.3 MOF growth

Copper nanocluster-decorated IDEs were used for MOF synthesis as described in section 6.1.3. By submerging a series of identical IDEs in the ligand solution and applying the potential for different amounts of time, the progress of the MOF growth could be assessed via SEM imaging. The top row labelled '0 minutes' in Figure 6.2 depicts only the nanoclusters on the IDE surface before any electrochemical synthesis, whilst the central row depicts the surface of the IDE after 10 minutes of electrochemical growth, and the bottom row the surface after 2 hours. The left-hand column shows images taken at 5K zoom, whilst the right-hand column shows images taken at 15K zoom.

By comparing the images of the IDEs at 0 minutes with those after 10 minutes, a change in surface morphology can already be seen. The spot-like nanoclusters visible in the 0 minutes images have been replaced by broader features with the same random but uniform distribution as the initial nanoclusters. This suggests that the larger crystallites have nucleated from the nanoclusters. After 2 hours, the surface features are bigger still, with the shapes less rounded

and more shard-like. Also of note is that the same crystallite growth is observed on the Pt of the IDEs and across the glass gaps, which is reflective of the even deposition of the nanoclusters on both of the electrode components.

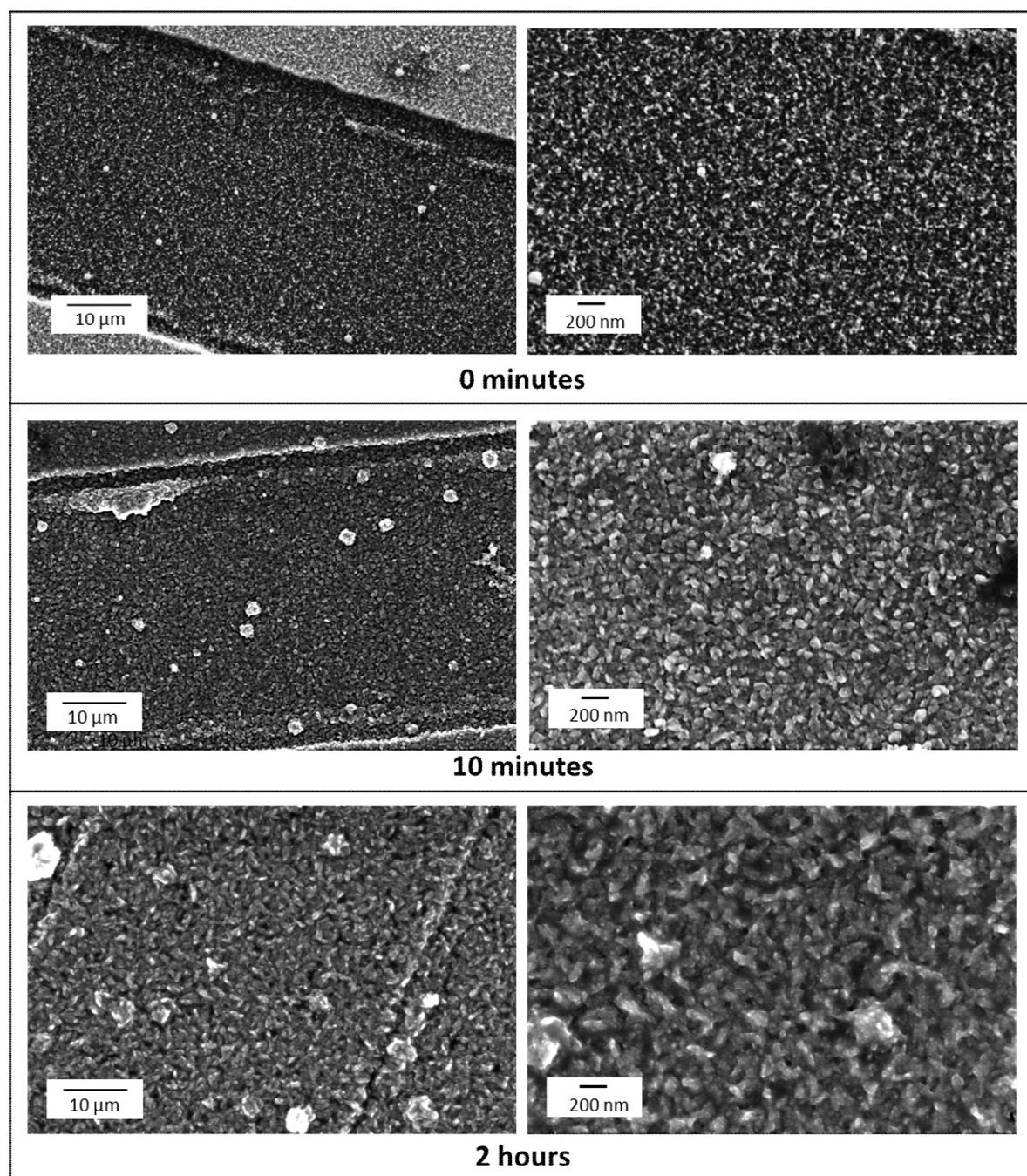


Figure 6.2: SEM images of copper nanocluster-decorated interdigitated electrodes after different electrochemical synthesis times. The top row depicts only nanoclusters, whereas $\text{Cu}_3(\text{HHTP})_2$ MOF crystals are visible for the samples after 10 minutes and 2 hours of electrochemical synthesis. Each column depicts the same sample imaged at different magnifications. As the synthesis time increases, the features on the IDE surface get larger as the MOF grows out from the nanoclusters.

The growth of the MOF is also reflected in how the measured resistance across the IDEs varies with electrochemical deposition time. The plot in Figure 6.3 was generated through measurement of the resistance between the contact pads of 5 separate IDEs after differing electrochemical synthesis times. The resistance decrease on increased electrochemical growth time is consistent with the MOF growing to bridge gaps between nanoclusters and then further to bridge the insulating gaps in the IDE, as illustrated schematically in Figure 6.1. The resistance of the sample that underwent 4 hours of electrochemical synthesis is however slightly higher than that of the 2 hours sample. It is expected that there will be a point beyond which the effect of copper nanoclusters being replaced by the less conductive MOF dominates over the increased bridging between clusters by the MOF. The increase in resistance between 2 and 4 hours suggests that this point lies between these two deposition time.

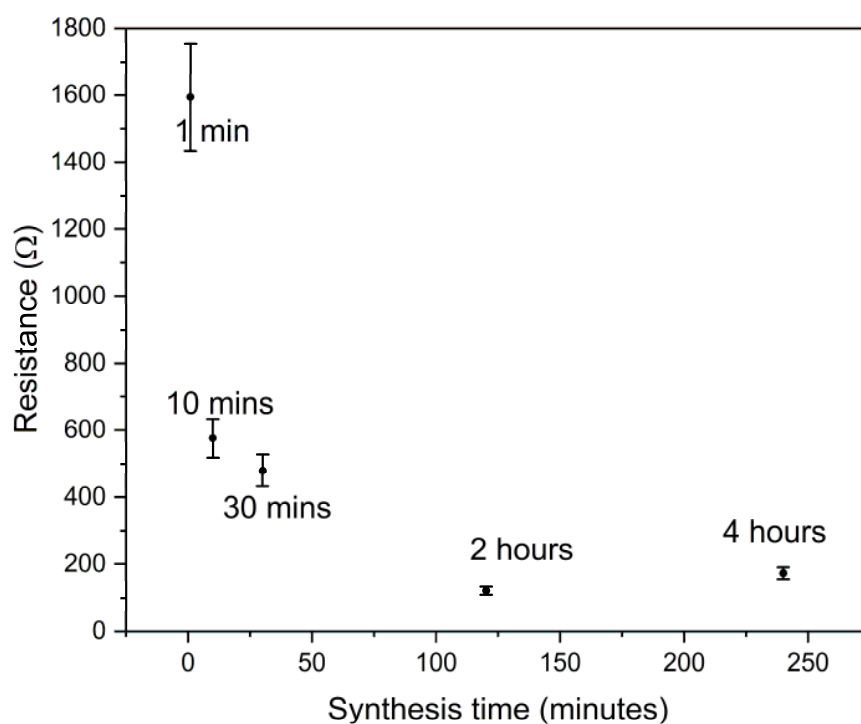


Figure 6.3: Plot of electrical resistance against MOF electrochemical synthesis time for 5 different copper nanocluster decorated IDEs. Largely, resistance decreases as synthesis time increases. This is consistent with conductive MOF growing to bridge the nanoclusters as the synthesis progresses. Error bars are estimates representing 10 % of the measured resistance.

6.4 Characterisation

As per the work detailed in chapter 5, sample characterisation is important for the work in this chapter to prove that the introduced method is successful in generating the desired MOF. As this method also uses nanoparticles covering small areas of substrate as the metal source for the MOF, the MOFs are synthesised in small amounts and are adhered strongly to the substrate. The XPS and Raman spectroscopy described in sections 6.4.2 and 6.4.3 respectively, could be performed with the MOFs in situ on the glass IDE substrates on which they were formed. However, for PXRD a larger volume of loose MOF powder was required. The synthesis was therefore scaled up using copper tape as opposed to copper nanoclusters, as described in the following section. Cyclic voltammetry was also performed to gain an insight into potential mechanisms of MOF formation.

6.4.1 Powder X-ray diffraction

Insufficient material could be obtained by scraping MOF off the IDEs for successful PXRD analysis. The synthesis was therefore scaled up using bulk copper tape (RS Pro conductive metallic tape, RS Components, UK) attached to a glass slide in order to obtain enough material to carry out PXRD. A 4cm × 4cm glass slide was covered in copper tape on both sides. This was used in place of the nanocluster-decorated IDE and connected to the 3-electrode set-up as described in section 6.1.3, where the potential of +0.435 V was applied for two hours. As observed for the copper nanocluster-decorated electrodes, the copper foil turned black during this time. The black material was then scraped off the tape with a spatula to yield sufficient powder for the PXRD data in Figure 6.4 to be obtained using a Rigaku Miniflex machine with a 1.54 CuK α source.

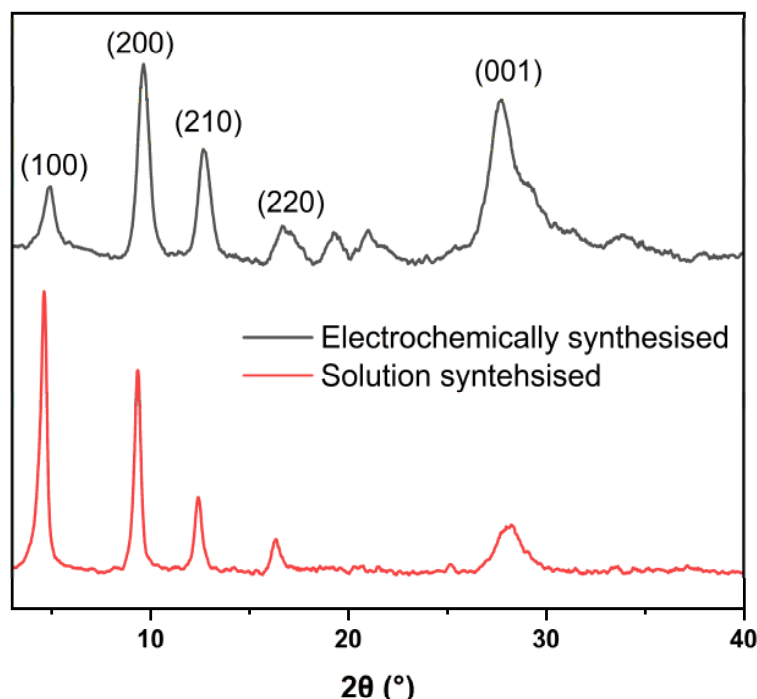


Figure 6.4: Powder X-ray diffraction pattern for $\text{Cu}_3(\text{HHTP})_2$ electrochemically synthesised from copper foil (grey) plotted against the PXRD scan of the same MOF synthesised via solution synthesis (red). The indexed (100), (200), (210), (220) and (001) peaks appear at the same 2θ values for MOF samples made from both methods, indicating that the same MOF is made in both cases.

Peaks are observed in the electrochemically synthesised sample at $2\theta = 4.95^\circ, 9.64^\circ, 12.67^\circ, 16.68^\circ$ and 27.76° . These peaks can be assigned to the (100), (200), (210), (220) and (001) planes respectively, as per the labels in Figure 6.4. When indexed to a hexagonal unit cell, the peaks correspond to lattice parameters of $a = b = 21.17 \text{ \AA}$, and $c = 3.21 \text{ \AA}$. In Figure 6.4, the PXRD data for the electrochemically synthesised MOF (grey) is plotted alongside the data for the same MOF synthesised via solution synthesis (red) as described in section 4.1.1. From this we can see that the positions of the indexed peaks are consistent with the peaks in the solution synthesised MOF. They are also consistent with the peak positions reported in literature.¹⁶⁰ The small peaks at 19.3° and 21.0° visible in the electrochemically synthesised PXRD scan (grey) cannot be assigned to any of the reaction mixture components or other potential products. It is therefore assumed that they arise due to impurities in the ‘conductive acrylic adhesive’ on the Cu tape used for the scaled-up electrochemical synthesis. We would therefore expect these peaks to be absent for the MOF prepared from Cu nanoclusters.

It is also worth noting the differences in relative intensities of the different PXRD peaks between the electrochemically synthesised and solution synthesised samples, which is suggestive of different crystal morphologies. In particular the relative heights of the (100) and (001) peaks indicate enhanced growth in the *c*-direction compared to that in the *ab* plane for the electrochemically synthesised sample. The effect of this on its performance as a chemiresistive sensor will be looked at in section 6.5.

6.4.2 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy, XPS, was able to be carried out in situ on the IDEs on which the MOF was synthesised, with no need to remove the MOF from the substrate. A K-alpha machine from Thermo Scientific, USA, was used. An electron neutraliser was used to prevent charge build up. The survey scan visible in Figure 6.5 shows the presence of the expected carbon, oxygen and copper elements in the MOF and is consistent with survey scans published in literature for $\text{Cu}_3(\text{HHTP})_2$.¹⁹⁵ The intense peaks at 532.1 and 285.1 eV can be attributed to photoelectrons emitted from the O 1s and C 1s sub-shells respectively. Also visible but less intense are peaks at 168.1 and 232.1 eV. These can be assigned to photoelectrons emitted from sulphur, indicating the presence of some residual TBMAMS electrolyte on the electrode surface. The peak at 402.0 eV is a N 1s peak that is present with similar intensity in the survey scan of the clean IDE. The Cu 2p peak around 940 eV will be looked at in more detail in Figure 6.6.

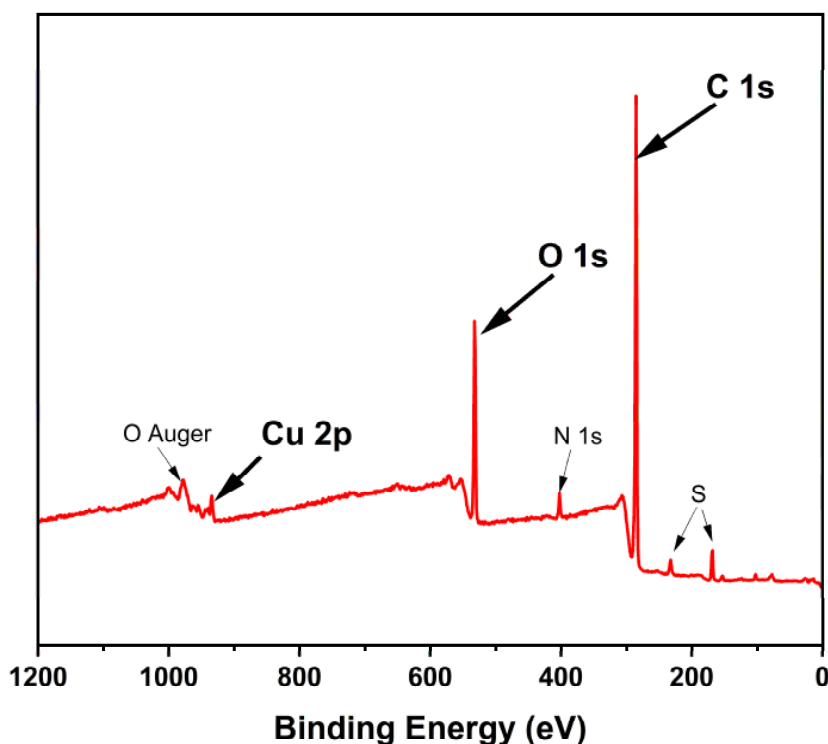


Figure 6.5: XPS survey scan for the $\text{Cu}_3(\text{HHTP})_2$ MOF synthesised via electrochemical synthesis from copper nanoclusters in situ on an interdigitated electrode substrate. Labelled in bold are the expected Cu 2p, O 1s and C 1s peaks from the elements present in the MOF. Also labelled are other peaks corresponding to S from the electrolyte and N from the substrate.

A higher resolution scan between 925 and 965 eV can reveal the finer structure in the Cu 2p region, Figure 6.6. Significant peak splitting for both the $2p_{3/2}$ and $2p_{1/2}$ peaks can be observed, indicating that the MOF contains both Cu^{2+} and Cu^+ species. The peaks at 932.4 and 952.2 eV can be assigned to the photoelectrons emitted from the $2p_{3/2}$ and $2p_{1/2}$ levels in Cu^+ or Cu, whilst the peaks at 934.5 and 954.2 eV can be assigned to the same sub-shells in Cu^{2+} . The presence of satellite peaks with similar splittings further confirms the presence of both copper ions.

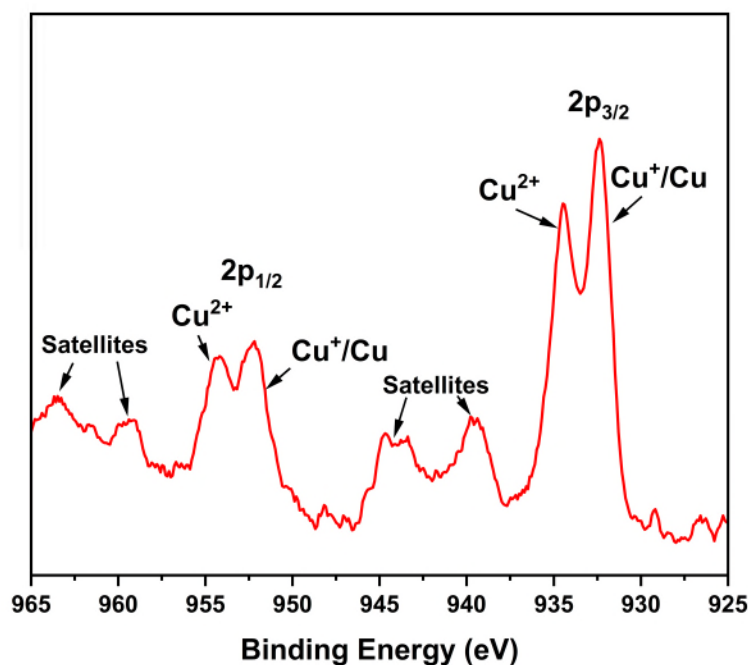


Figure 6.6: Narrow area XPS scan of the Cu 2p region for $\text{Cu}_3(\text{HHTP})_2$ on glass inter-digitated electrodes. Each of the $2p_{3/2}$ and $2p_{1/2}$ peaks are split into Cu^+/Cu and Cu^{2+} peaks. Similar splittings are visible in the satellite peaks at slightly higher binding energies.

6.4.3 Raman spectroscopy

Raman spectroscopy was carried out with the $\text{Cu}_3(\text{HHTP})_2$ still adhered to the glass IDE substrates on which they were synthesised. A System 1000 machine from Renishaw, UK was used. The resulting spectrum for the electrochemically synthesised MOF can be seen in red in Figure 6.7. It has been plotted against the trace for the HHTP ligand starting material (blue) and the same $\text{Cu}_3(\text{HHTP})_2$ MOF synthesised via solution synthesis and drop-cast onto the same IDE substrates (grey). The spectra show the presence of peaks in the MOF scans that are not observed in the spectrum for the HHTP organic starting material. The spectra have been artificially offset in y for clarity.

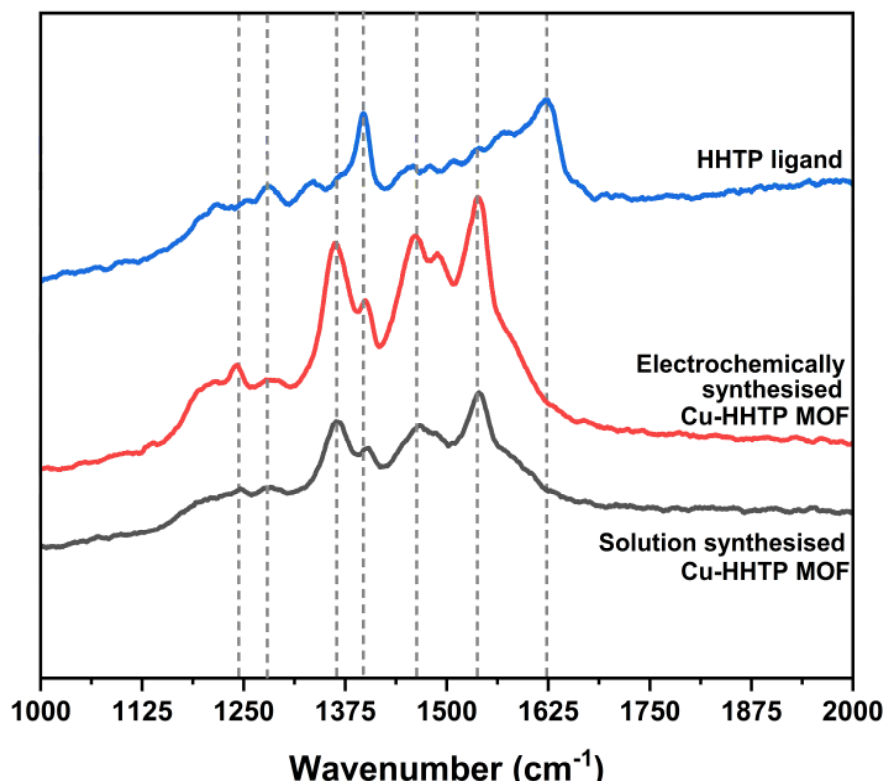


Figure 6.7: Raman spectra of $\text{Cu}_3(\text{HHTP})_2$ MOF synthesised via electrochemical synthesis from copper nanoclusters (red) and conventional solution synthesis methods (grey) compared to Raman spectrum for the HHTP ligand on the same substrate (blue). Peaks for the MOF traces appear at the same wavenumbers, and both traces differ from that of the ligand. This indicates that the same substance is formed during the electrochemical and solution synthesis methods, and that this cannot be due to ligand deposition on the IDE surface.

On looking at the Raman spectrum for the HHTP ligand in Figure 6.7 (blue), the two sharpest peaks are observed at 1398 and 1620 cm^{-1} . On transformation to the MOF, the 1620 cm^{-1} disappears, whilst the 1398 cm^{-1} peak remains in the spectra for the MOF samples made from both methods but with a lower intensity. New peaks arise at 1363, 1461 and 1542 cm^{-1} in the spectra for the MOFs. The appearance of peaks at the same wavenumbers for the $\text{Cu}_3(\text{HHTP})_2$ samples made from solution and electrochemical synthesis reinforces the conclusion that the same MOF is made from both methods. The marked difference between the MOF traces and the trace for the HHTP ligand indicates that the ligand has undergone chemical changes to form a new compound. The peaks observed in Figure 6.7 are in the region typical of aromatic systems, known constituents of the desired MOF. To assign the peaks to specific bonds, DFT calculations could be performed.

6.4.4 Cyclic voltammetry

Cyclic voltammetry, CV, was performed to investigate the redox processes involved in formation of the MOF. An IDE with copper nanoclusters deposited on it was submerged in a solution of the ligand and electrolyte and the potential was ramped from -0.80 V to +1.20 V in steps of 0.00244 V with a speed of 0.02 V s⁻¹. The two sides of the IDE were connected for this experiment, and the current flowing between the IDE working electrode and the reference electrode is recorded as the voltage is changed. The resulting current vs potential plot is given in Figure 6.8.

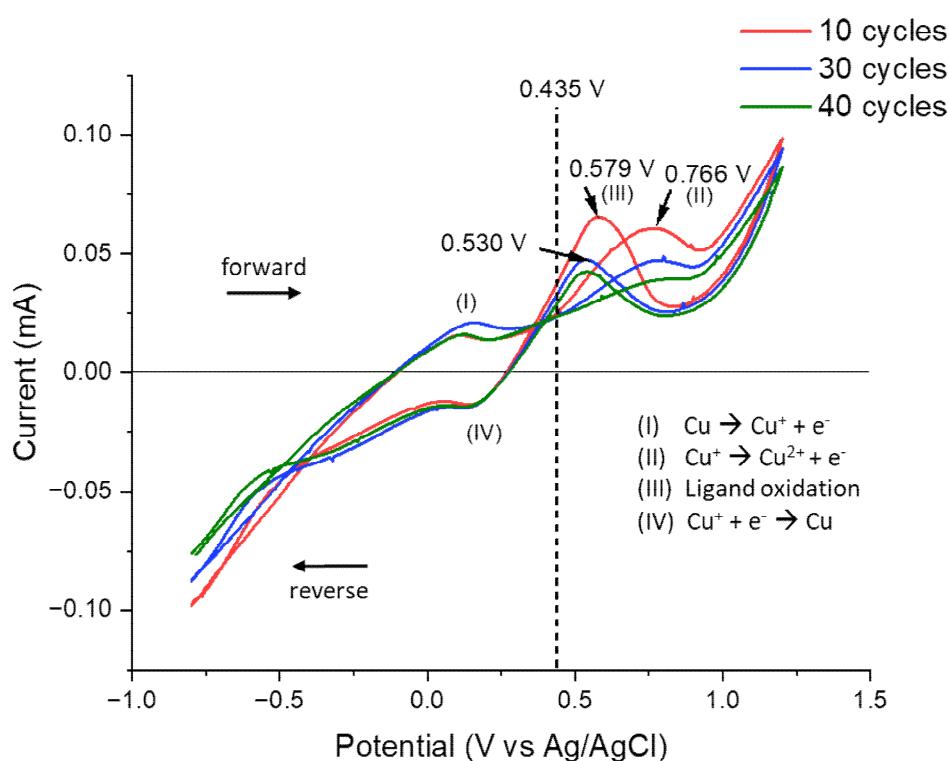


Figure 6.8: Cyclic voltammogram for a copper nanocluster-decorated electrode in a solution of HHTP ligand and electrolyte. Potential was ramped from -0.8 V to +1.2 V for 40 cycles. Peaks in the forward direction occur at 0.15 V and 0.77 V. Peaks in the reverse direction appear at 0.56 V and 0.14 V. The positive current peak at 0.56 V that occurs as Cu^{2+} ions on the IDE are reduced to Cu^+ ions in order to oxidise the ligand.

In the forward direction, peaks occur at 0.148 and 0.766 V. The first of these is assumed to be due to the oxidation of metallic Cu to Cu^+ ions, whilst the second is likely due to the further oxidation of Cu^+ to Cu^{2+} . In the reverse direction, we observe a positive current peak at 0.579 V and a negative peak at 0.140 V. The peak at 0.140 V can be attributed to the reduction of Cu^+ ions back to Cu metal. The peak at 0.579 V that crosses over the forward scan, indicates that electrons are being donated to the electrode despite the fact that the potential is being decreased. We postulate that this peak corresponds to Cu^{2+} ions oxidising the HHTP molecules. On the forward scan Cu^{2+} ions form which can then participate in the step-wise oxidation of the hydroxy-substituted ligand to the semiquinone species. Each Cu^{2+} ion can accept one electron, forming Cu^+ , and so oxidise one dihydroxy group to the corresponding semiquinone radical, Figure 2.18. Since this involves the copper species on the electrode accepting electrons which can then be transferred to the circuit, the peak presents in the positive current direction crossing over the forward traces. As the solution is degassed with N_2 flow prior to the experiment, O_2 dissolved in the solution cannot participate in ligand oxidation. The CV suggests that the maximum rate of ligand oxidation occurs at a potential of 0.579 V, with a lower rate at higher potentials in the reverse direction due to the lower stability of the Cu^+ ion in this environment.

The insights from the CV inform the mechanism of MOF formation with this method. It is expected that the MOF forms via the following sequence of steps:

1. Oxidation of the metal to the Cu^+ then Cu^{2+} species due to the applied potential.
2. Deprotonation of the ligand in solution.
3. Oxidation of the ligand by Cu^{2+} ions on the IDE, forming Cu^+ .
4. Deprotonation of the ligand and combination with metal ions to irreversibly form the MOF.

The 0.435 V applied for MOF formation, as marked by the dashed line in Figure 6.8, is approximately at the point where the $\text{Cu}^+/\text{Cu}^{2+}$ current increase begins. It is therefore likely that this is the minimum potential that could be used to trigger formation of the Cu^{2+} ions, whilst minimising the oxidation rate, which is desirable for formation of larger crystals.

6.5 Sensing behaviour

The MOF-decorated electrodes were submerged in acetone overnight and dried for 10 minutes on a hot plate at 80 °C before being put into a custom-built sensing chamber. A potential difference of 1V was applied across the IDEs and the current flow was recorded in real time using a digital multimeter. The current flowing was monitored as the sensors were exposed to concentrations of NH_3 gas between 5 and 1 ppm for 60 s each, with recovery times of 20 minutes for the 5 ppm exposures. A constant flow rate of 500 sccm was maintained and a dry N_2 carrier gas was used.

A typical resistance response plot can be seen in Figure 6.9 - top, which was obtained from a sensor that underwent 2 hours of electrochemical synthesis. In this figure we see a reversible resistance increase on exposure to ammonia. As NH_3 is a strong electron donor, the resistance increase on exposure to NH_3 is consistent with the MOF behaving as a p-type semiconductor. The change in resistance on exposure as a percentage of the initial resistance is then plotted against concentration to produce the calibration plot in Figure 6.9 – bottom, no baseline correction was required. The gradient of this plot gives the sensor sensitivity as 0.154 ± 0.006 % ppm^{-1} . The root mean square, RMS, of the baseline noise is 0.00813 %. By using the sensitivity to calculate the analyte concentration that would give a sensing response with magnitude 3 times greater than the baseline noise, a calculated limit of detection of 158 ± 6 ppb is obtained.

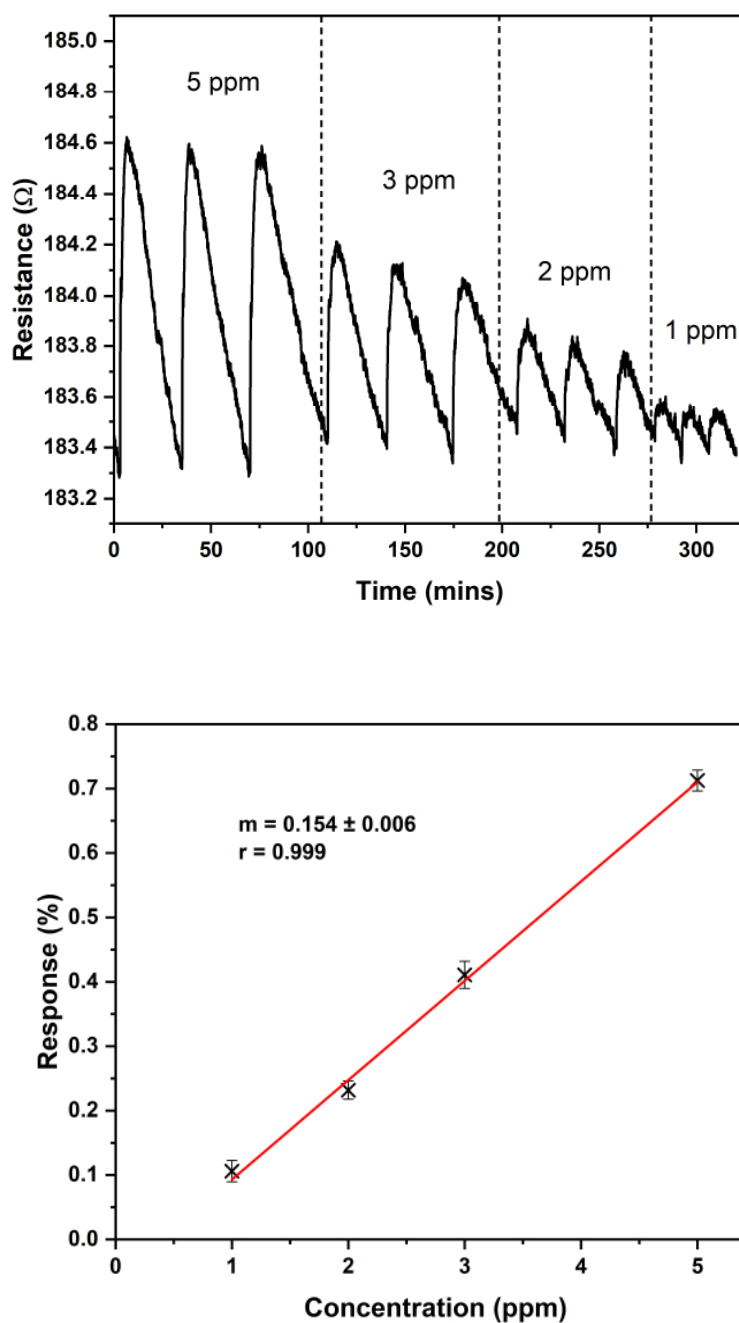


Figure 6.9: *Top* – The reversible resistance increases of a sensor exposed to NH_3 gas with concentrations between 5 and 1 ppm for 60 s. *Bottom* - Plot to show the linear relationship between response % and NH_3 concentration. The gradient of this plot gives the sensitivity of the sensor. Results are from a $\text{Cu}_3(\text{HHTP})_2$ MOF sensor generated from 2 hours of electrochemical synthesis. The linearity of sensing response with increasing concentration is superior to that obtained with solution synthesised MOF sensors.

The reversible resistance increase on exposure to NH_3 gas is consistent with the response shape for the same MOF synthesised via solution synthesis (section 4.2.3). The calculated limit of detection of the sample prepared via electrochemical synthesis (0.158 ± 0.006 ppm) is of a similar magnitude to that of the $n\text{-Cu}_3(\text{HHTP})_2$ sensor made from solution synthesis (0.13 ± 0.01 ppm). It can be observed however, that the electrochemically synthesised sample shows a significantly improved linearity of relationship between response % and analyte concentration, with a Pearson's r of 0.999 for the electrochemically synthesised sample, compared to $r = 0.991$ for the solution synthesised $n\text{-Cu}_3(\text{HHTP})_2$ sensor. Furthermore, the variance in response magnitudes between exposures of the same concentration is far smaller for the electrochemically synthesised sensor, as depicted by the much smaller error bars visible in Figure 6.9 compared to the analogous plot in chapter 4 (Figure 4.5). This renders the electrochemically synthesised sample a more reliable real-world sensor, as an analyte concentration inferred from a given response % can be more accurately determined.

The response to NO_2 gas was also probed using the same sensor and the same experimental conditions. As was observed for the solution synthesised $\text{Cu}_3(\text{HHTP})_2$ sensors, exposure to NO_2 resulted in irreversible resistance decreases, Figure 6.10. This indicates that the NO_2 is interacting with the framework in the same way as was described in section 4.5. The irreversible nature of the interaction means that the magnitude of the resistance decrease decays rapidly on repeated exposures to the same concentration of analyte gas. As such no sensitivity or limit of detection could be ascertained. The decrease in resistance continues after the NO_2 exposure stops, but with an increasingly shallow gradient. This can be seen more clearly in the lower graph of Figure 6.10 which depicts a single 5 ppm NO_2 exposure.

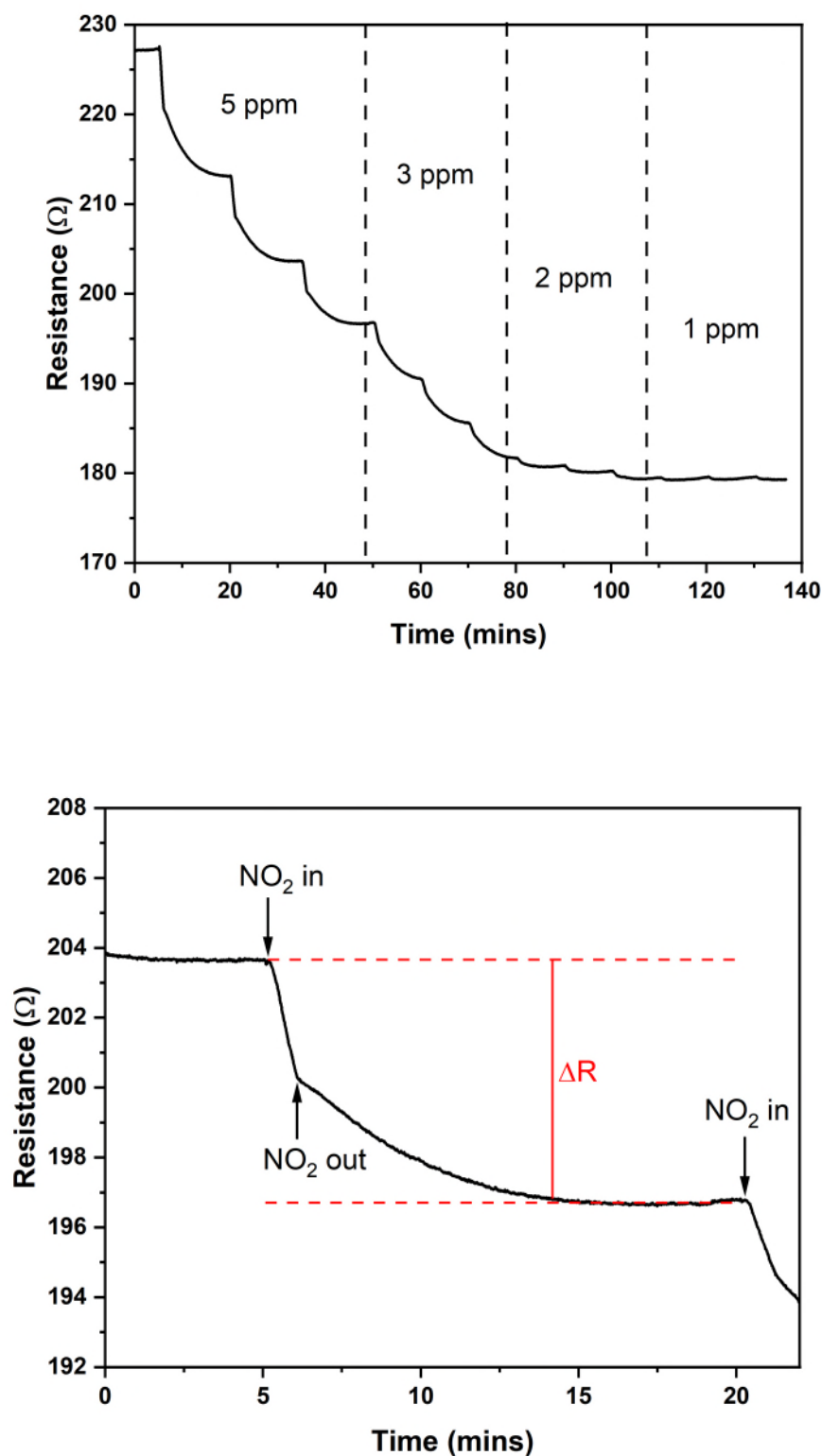


Figure 6.10: *Top* - The resistance response of an electrochemically synthesised $\text{Cu}_3(\text{HHTP})_2$ sensor exposed to NO_2 gas with concentrations between 5 and 1 ppm for 60 s. *Bottom* – Enlarged plot of a single 5 ppm NO_2 exposure indicating the start and end points of the exposure. Annotations in red show how the change in resistance is measured.

When ΔR is measured as depicted in Figure 6.10, the first 5 ppm exposure leads to a percentage change in resistance of 3.4 %. This change is significantly lower than the 19.6 % and 8.7 % for the α -Cu₃(HHTP)₂ and n -Cu₃(HHTP)₂ sensors tested in chapter 4. This could be rationalised by considering the sensing mechanism discussed in section 4.4, alongside comparing the morphology of the electrochemically and solution synthesised samples. In section 4.4 it was concluded that NO₂ is likely to interact with lone pairs on the ligand oxygen atoms. These would be most accessible for the ligands on the outer edges of the crystals. The rod-like crystals would therefore have the highest concentration of easily accessible oxygen lone pairs. The flake-like crystals of the n -Cu₃(HHTP)₂ sample would have fewer accessible external ligands due to the reduced thickness of the MOF crystals, whilst the electrochemically synthesised samples would have fewer still due to the dense packing of the flake-like crystals.

6.6 Conclusion

A method to electrochemically grow Cu₃(HHTP)₂ from pre-patterned copper nanoclusters has been presented. The described protocol allows us to generate a uniform distribution of the MOF in situ on the IDEs required for chemiresistive gas sensing. SEM imaging indicates that significant MOF growth occurs within 10 minutes of applying the potential, which is corroborated by a decrease in measured resistance across the electrodes. A sensor made after 10 minutes of electrochemical growth is reported to detect NH₃ gas with a limit of detection of 158 ± 6 ppb. The method offers advantages in terms of uniformity of chemiresistive sensing medium, control of MOF growth, and reduced post-growth processing requirements.

The only chemiresistive Cu₃(HHTP)₂ NH₃ sensor with a calculated limit of detection reported in literature is that fabricated by Yao et al. using a spray layer-by-layer deposition method. They reported an LOD of approximately 500 ppb, making the sensor fabricated in this chapter

superior.¹⁹⁶ Moreover, our calculated LOD of 158 ppb is competitive with the LODs quoted for chemiresistive sensors fabricated from conducting polymers and metal-oxide semiconductors.⁷ However, as discussed in section 3.3.2, it should be noted that factors such as the gas flow rate, exposure time and sensing chamber geometry have significant effects on the sensing responses and limits of detection. Comparisons between sensors made by different research groups should therefore be treated with caution, as experimental conditions are rarely consistent. The electrochemically-synthesised sensor discussed here can however be compared to the $\text{Cu}_3(\text{HHTP})_2$ sensors made from powdered MOF described in section 4.2.3 which were analysed under identical conditions. On comparing the sensing results in Figure 6.9, to those in Figure 4.5, it can be observed that the electrochemically-synthesised MOF sensor results in a more linear response % against analyte concentration plot which leads to lower uncertainties in the sensitivity and limit of detection. This means that the concentration of analyte can be more accurately calculated from the electrochemically-synthesised sensor. Moreover, the electrochemically synthesised sample is significantly more robust, in that the MOF could not be removed from the IDE through sonication in ethanol, whilst macroscopic amounts of the powdered MOF came off the IDE each time the solution synthesised sensor was submerged in then removed from an ethanol solution.

Chapter 7

Templated synthesis of conductive MOFs for hierarchically porous sensors

In this chapter I will describe a method to synthesise all four metal-organic frameworks previously discussed in this thesis, $\text{Cu}_3(\text{HHTP})_2$, $\text{Cu}_3(\text{HITP})_2$, $\text{Ni}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HITP})_2$, in an inverse opal morphology using polystyrene nanospheres. The motivation and inspiration for these experiments will be discussed in section 7.1 and the methodology will be described in section 7.2. SEM images of the samples of the four different MOFs will be given in section 7.3.1, the EDX results will be discussed in section 7.3.2 and the results of XPS characterisation will be covered in section 7.3.3. The inverse opal MOFs produced in this method were used to make chemiresistive sensors and their responses to NH_3 and NO_2 analyte gases were tested. The results of these experiments are discussed in section 7.4. This section includes a comparison of the sensing ability of the hierarchically porous MOF structures detailed in this chapter, with those of the MOF sensors discussed in chapter 4.

7.1 Context

The morphology of conductive triphenylene-based MOFs has been reported to be a significant factor determining the success of MOF-functionalised electronic materials. The first study in which the morphology of $\text{Cu}_3(\text{HHTP})_2$ was deliberately manipulated used different amounts of NH_3 and pyridine modulators to change the crystals from rods to flakes.¹⁶⁸ In chapter 4 of this thesis, section 4.2.3, $\text{Cu}_3(\text{HHTP})_2$ with a flake-like morphology was found to have a higher sensitivity to NH_3 gas than the rod-like crystals of the same MOF. Other published work has focused on the role of triphenylene-based MOF morphology on capacitive

performance. In 2021, Dincă et al. concluded that the capacitive performances of $\text{Ni}_3(\text{HITP})_2$ MOF samples were more affected by morphology and crystal agglomeration than by conductivity.¹⁹⁷ Similarly, in subsequent work by Forse et al. the capacitive performance of $\text{Cu}_3(\text{HHTP})_2$ was found to be enhanced when flatter MOF crystals were used.¹⁹⁸

This well-established relationship between crystal morphology and electronic device performance, inspired me to consider further ways of manipulating the structures of the MOFs featured in this thesis. The formation of hierarchically porous MOF structures via supramolecular templating has been reported for many 3D MOFs.¹⁹⁹ In 2012, Kitagawa et al. described a method of producing an inverse opal structure of an aluminium naphthalene dicarboxylate framework from an inverse opal aluminium template. The aluminium structures were formed from polystyrene bead arrays treated with an acidic aluminium butoxide solution, and then converted to the MOF via microwave treatment in the presence of the ligand.²⁰⁰ Formation of inverse opal structures of a 2D conductive MOF was subsequently reported by Miao et al.. Polystyrene nanospheres were mixed with $\text{HATP} \cdot 6\text{HCl}$ and deposited onto ceramic electrodes.¹⁹⁰ An alkaline solution of CuSO_4 was then drop-cast onto the dry nanosphere/ligand mixture, forming the $\text{Cu}_3(\text{HITP})_2$ MOF within seconds. Tetrahydrofuran, THF, was used to dissolve the polystyrene nanospheres to leave the inverse opal structured MOF. The authors also report that when used as a chemiresistive sensor, the nanostructured MOF performed as a better sensor to H_2S than an analogous non-nanostructured $\text{Cu}_3(\text{HITP})_2$ sensor, although responding irreversibly in both cases.

In this chapter, the synthesis first described by Miao et al. is modified and applied to other conductive MOFs, resulting in inverse opal structures of 3 conductive MOFs that have not been reported with this structure previously, $\text{Cu}_3(\text{HHTP})_2$, $\text{Ni}_3(\text{HITP})_2$ and $\text{Ni}_3(\text{HHTP})_2$, as well as $\text{Cu}_3(\text{HITP})_2$. The sensing response of the 4 nanostructured MOFs to NH_3 and NO_2 are

investigated and assessed relative to analogous sensors made with non-microstructured MOFs. This comparison can give us an insight into the extent to which diffusion limits the sensing response, and whether altering the morphology in this way could affect the sensing performance in terms of magnitude or reversibility.

7.2 Materials and methods

The principles of this method are represented schematically in Figure 7.1. The first step involves depositing a mixture of ligand and nanospheres onto an electrode via drop-casting, Figure 7.1 (a). An alkaline solution of a metal salt is then deposited on top, allowing the metal ions to react with the ligand to form the MOF in the areas not occupied by the nanospheres, Figure 7.1 (b). The final stage involves submerging the electrode in tetrahydrofuran (THF) to dissolve the nanospheres, leaving an inverse opal structure of the MOF, Figure 7.1 (c).

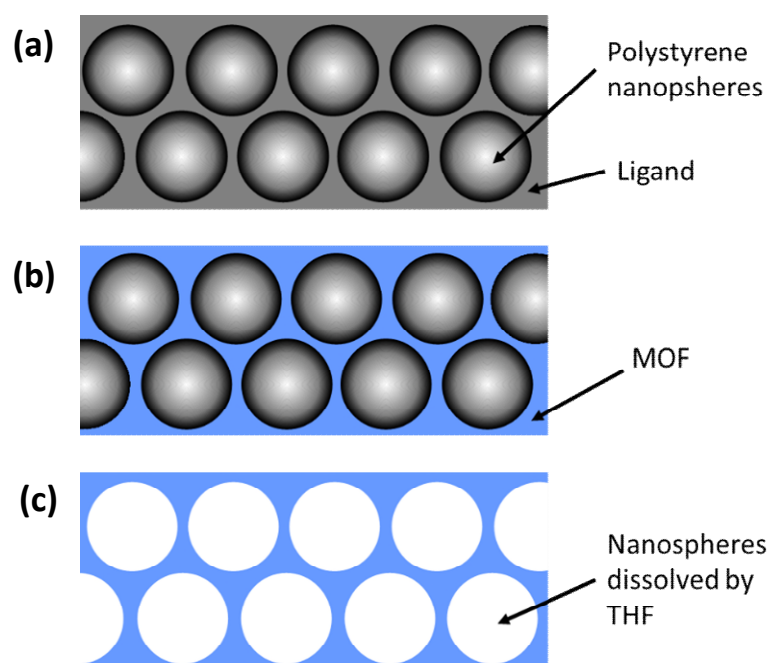


Figure 7.1: Schematic illustration for the formation of inverse opal structures of conductive MOFs via templated synthesis using polystyrene nanospheres. **(a)** Ligand surrounds polystyrene nanospheres. **(b)** MOF forms around the nanospheres on addition of metal salt solution. **(c)** The inverse opal MOF structure remaining after dissolution of the nanospheres with THF.

Two polystyrene nanosphere solutions with a 1.5 mg mL^{-1} concentration were made up in deionised water. The nanospheres were purchased from Sigma-Aldrich, USA as an aqueous suspension. The mean diameters of the particles is $0.3 \text{ }\mu\text{m}$. To one of the nanosphere solutions 2,3,6,7,10,11-hexahydroxytriphenylene (TCI, Japan) was added to form a 7 mg mL^{-1} , 10.8 mM , solution with respect to the HHTP. To the other nanosphere solution, 2,3,6,7,10,11-hexaaminetriphenylene hexachloride was added to produce a 10 mg mL^{-1} , 9.3 mM , solution with respect to the HATP.6HCl. Two further solutions were made up, one comprising copper(II) sulphate pentahydrate (Fisher Scientific, UK), and the other nickel acetate tetrahydrate (Acros Organics, USA). Solutions containing 9.53 mL of deionised water and 0.47 mL ammonia solution (19.4 M , Fisher Scientific, UK) were made up, to which the metal salt was added to form 0.13 mM solutions of the metal salts.

Interdigitated electrodes with $5 \text{ }\mu\text{m}$ gap sizes (Micrux Technologies, Spain) were placed on a hot plate at $60 \text{ }^{\circ}\text{C}$. To make the $\text{Cu}_3(\text{HHTP})_2$ MOF, one $10 \text{ }\mu\text{L}$ drop of the HHTP/nanosphere solution was dropped onto the hot electrode. After 5 minutes of drying, two $5 \text{ }\mu\text{L}$ drops of the alkaline copper sulphate solution were drop-cast on top. To make the $\text{Cu}_3(\text{HITP})_2$ MOF, $10 \text{ }\mu\text{L}$ of the HATP/nanosphere solution was drop-cast onto the hot electrode. After drying on the hot plate (5 minutes), one $10 \text{ }\mu\text{L}$ drop of the alkaline copper sulphate solution was drop-cast on top. To make the $\text{Ni}_3(\text{HHTP})_2$ sample, again a singular $10 \text{ }\mu\text{L}$ drop of the HHTP/nanosphere solution was drop-cast onto the hot electrode, followed by two $10 \text{ }\mu\text{L}$ drops of the alkaline nickel salt solution after 5 minutes of drying. Similarly, the $\text{Ni}_3(\text{HITP})_2$ MOF was synthesised from one $10 \text{ }\mu\text{L}$ drop of HATP/nanosphere solution followed by 5 minutes of drying and then $3 \times 10 \text{ }\mu\text{L}$ drops of the alkaline nickel salt solution.

After a further 30 minutes of drying on the hot plate at $60 \text{ }^{\circ}\text{C}$, the four samples were allowed to cool to room temperature. They were then placed in narrow 8 mL vials to which 3 mL of

THF was added. The vials were left overnight, after which the IDEs were removed from the THF and dried for 20 minutes on a hot plate at 60 °C.

7.3 Characterisation

The MOF sensors fabricated as described in section 7.2 were characterised via SEM, EDX and XPS. Analysis with all of these techniques was carried out with the MOFs still adhered to the inter-digitated electrode substrates that they were synthesised on. This analysis is therefore reflective of the conditions of the MOF during the sensing experiments to be described in section 7.4.

7.3.1 Scanning electron microscopy

SEM imaging of the four different MOFs reveals inverse opal structures with slight differences in morphology. Representative images are given in Figures 7.2 and 7.3. For all four samples, spherical holes previously occupied by polystyrene nanospheres can be observed. Solid material that is resistant to the THF used to dissolve the nanospheres remains around these hollow regions. Of the four samples, that of $\text{Cu}_3(\text{HHTP})_2$ shows the least rigid inverse opal structure, Figure 7.2 – top, whilst the inverse opal structure for the $\text{Ni}_3(\text{HITP})_2$ sample is continuous over the whole of the depicted region, Figure 7.3 – bottom. Looking more closely at the morphology of the material making up the inverse opal structures, it can be observed that the HHTP-based MOFs, Figure 7.2, are comprised of angular features arranged around the regions previously occupied by the nanospheres. The diameters of these angular features are no more than 60 nm when viewed as a cross-section for both HHTP MOFs. Some regions of more continuous solid material are visible over larger areas

representing partial surfaces of the spheres, indicating that the presence of the spheres during the synthesis is directing the morphology and growth of the MOF.

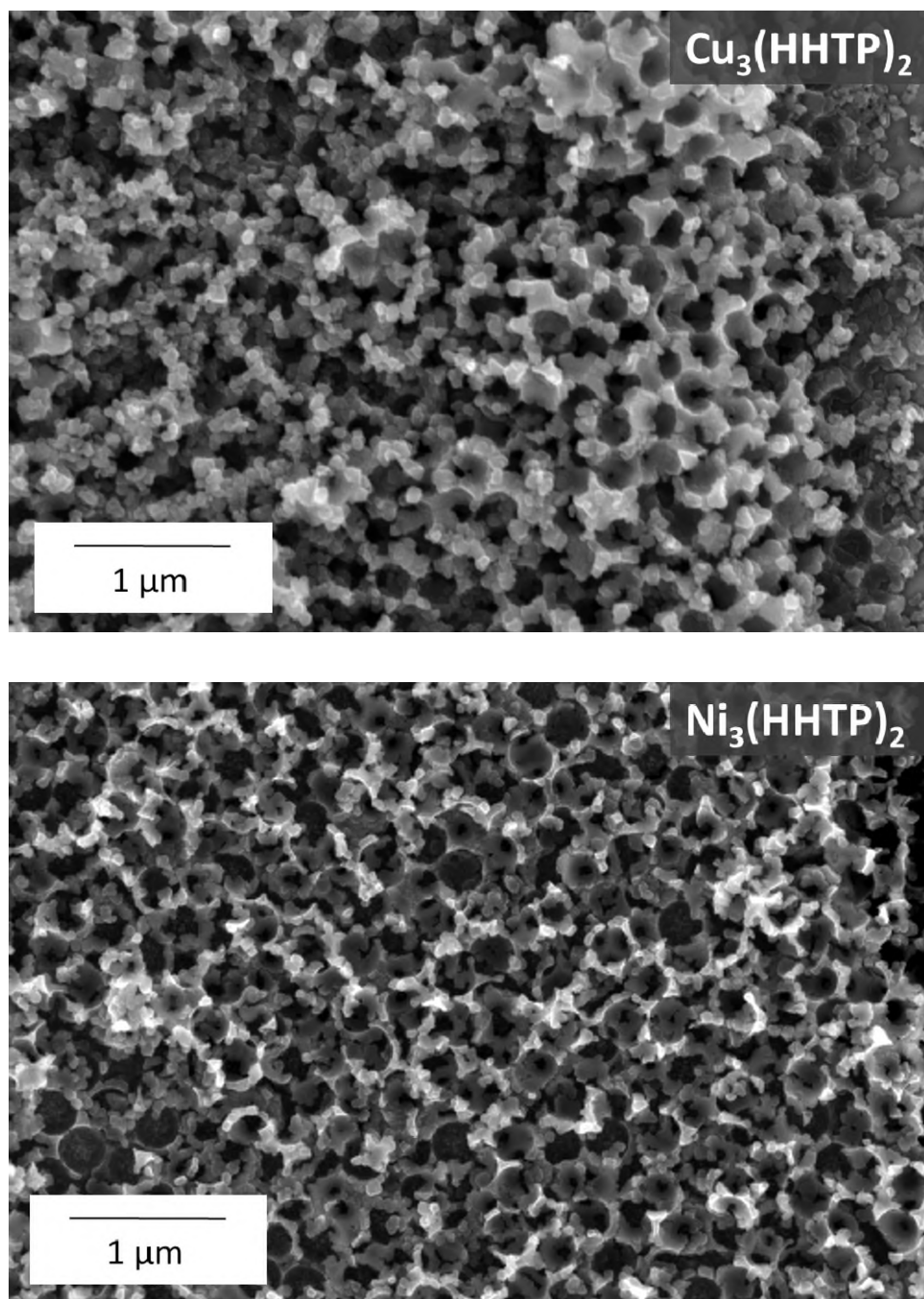


Figure 7.2: *Top* – SEM image of $\text{Cu}_3(\text{HHTP})_2$ synthesised around a polystyrene nanosphere template. *Bottom* – SEM image of $\text{Ni}_3(\text{HHTP})_2$ synthesised around a polystyrene nanosphere template. Inverse opal structures are visible in both images, indicating that the MOFs have grown around the nanosphere templates. The $\text{Ni}_3(\text{HHTP})_2$ MOF has taken to the templated synthesis method better, with a more extensive inverse opal structure visible for that sample.

SEM imaging of the analogous HTP-based MOFs revealed further inverse opal structures, Figure 7.3. For the $\text{Cu}_3(\text{HTP})_2$ sample, Figure 7.3 – top, there are fewer regions where the MOF has grown smoothly and continuously around the nanosphere template, with only a couple of smooth grey partial nanosphere shell regions. This indicates that MOF has not grown well on the surfaces of the ligand-coated nanospheres that are in contact with the electrode, with MOF-like material largely only visible bridging the nanosphere vacancies rather than underneath them as well. In contrast to the HHTP MOFs where any non-continuous shells are made up of angular features with aspect ratios close to one, the $\text{Cu}_3(\text{HTP})_2$ sample shows rod-like features, some spanning the distances between circular hollows left by the nanospheres with lengths of the order of 100 nm. The persistence of rod-like features despite the nanosphere template, suggests that the favourability for growth in one particular dimension is strong for this MOF or more likely, that the growth of crystals is favoured over nucleation of new crystals for the synthesis of this MOF in this way.

The appearance of the $\text{Ni}_3(\text{HTP})_2$ sample, as depicted in Figure 7.3 – bottom, shows a further contrasting morphology. This image shows the highest proportion of continuous smooth inverse opal shells of the four MOFs discussed, indicating that growth of the $\text{Ni}_3(\text{HTP})_2$ MOF is most easily directed by the presence of the nanospheres. In contrast to these smooth regions previously in direct contact with the nanospheres, the outer surfaces of the smooth areas are noticeably rougher with densely packed nm-sized protrusions.

A number of factors are relevant in determining the success of this method in generating the MOFs, and the morphology of the MOF formed. These include the miscibility of the ligand and the nanosphere solution, the rate of deprotonation of the ligand on addition of the alkaline metal salt solution (affected by the pH), the rate of coordination of the metal ion to the deprotonated ligand and the extent to which the ligand remains coated on the nanospheres as

the ligand/nanosphere solution dries. Whilst the morphologies of the two HHTP MOFs resemble each other on the scale smaller than the inverse opal arrangement, the two HITP MOFs differ more significantly, indicating that it is not simply the differences in the ligands that are responsible for the contrasting morphologies. Comparing the SEM images given in this chapter, with those for the same MOFs synthesised via conventional solution synthesis methods, chapter 4, we see that the differences in sub-inverse opal morphologies are indeed reflective of the solution synthesised MOF morphologies in most cases. However, the features are consistently smaller for the MOFs synthesised in this chapter compared to those in chapter 4, as expected for the rapid method described here. The $\text{Cu}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HHTP})_2$ solution synthesised samples are rod-like crystals with hexagonal cross sections. The features observed in Figure 7.2 resemble these in their cross section, but the growth in the favoured direction has been suppressed, likely due to the constraints imposed by the close proximity of the nanospheres. Similarly, the rough surface protrusions observed for the $\text{Ni}_3(\text{HITP})_2$ MOF in Figure 7.3 – bottom, are reflective of the fine crystals imaged in Figure 4.7 – bottom. The features observed for the $\text{Cu}_3(\text{HITP})_2$ crystals however, do not resemble the solution synthesised version as closely, with the rod-like features visible in the templated synthesis not visible amongst the fine crystals and with no obvious favourable growth dimensions as observed in the solution synthesised sample, Figure 4.7 – top. The net impact of the inverse opal microstructure and the template-induced changes to particle morphology on the chemiresistive sensing performances will be discussed later in this chapter.

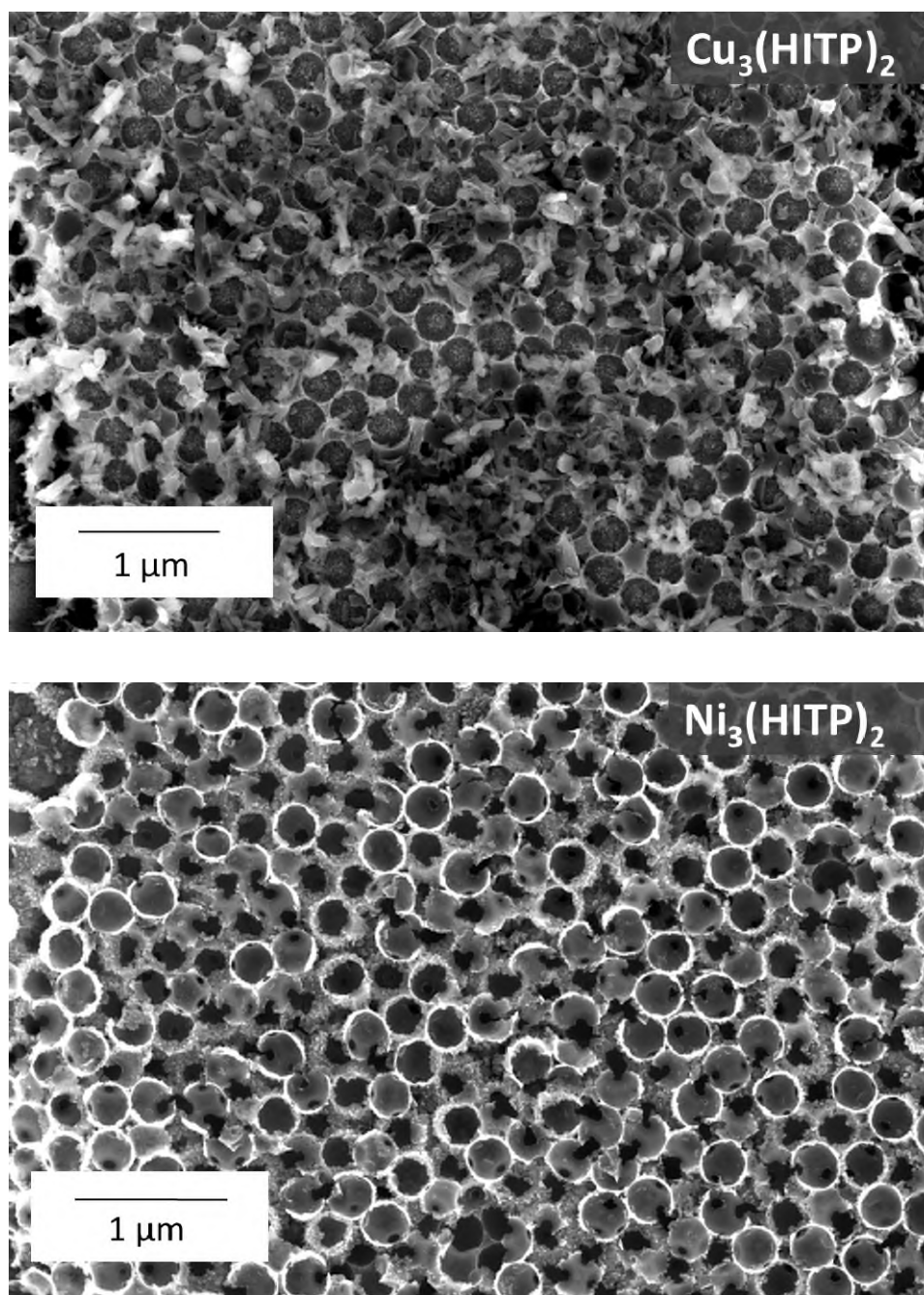


Figure 7.3: *Top* – SEM image of $\text{Cu}_3(\text{HITP})_2$ synthesised around a polystyrene nanosphere template. MOF particles are visible bridging the vacancies previously occupied by nanospheres. Some rod-like features are visible despite the nanosphere template used. *Bottom* – SEM image of $\text{Ni}_3(\text{HITP})_2$ synthesised around a polystyrene nanosphere template. Shells of solid material surrounding the spaces previously occupied by nanospheres are clearly visible. The outer surfaces of the shells are rough with densely packed nm-sized protrusions.

7.3.2 Energy dispersive X-ray analysis

Energy dispersive X-ray, EDX, mapping experiments were performed to analyse the elemental composition of the material on the electrodes. The results of these experiments can be seen in Figures 7.4 and 7.5. By inspecting the chemical composition spectra for the 4 MOFs, the presence of the expected Cu, Ni, C, N and O elements can be confirmed. The SEM images taken of the mapped areas depict only material with the inverse opal structures, with no evidence for the presence of other crystalline phases or amorphous material. This indicates that the material with the inverse opal structure contains both metal and linker components, which suggests MOF formation has been successful.

In addition to the expected elements present in the desired MOFs, the EDX composition spectra show that Si, Na, K, Pt, Cl and S are present. Si, Na and Pt are all components of the glass IDE substrates, but the reason for the presence of K is unknown. Whilst some Cl and S is likely present in the IDEs too, Cl and S are also present in the starting materials for some of the MOFs. S is present in the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ used to produce both the $\text{Cu}_3(\text{HHTP})_2$ and $\text{Cu}_3(\text{HITP})_2$ MOFs. By inspecting the spectra in Figures 7.4 and 7.5, it can be seen that S is indeed present in the EDX maps of both the Cu-containing MOFs, with smaller peaks not at a high enough concentration to be labelled by the EDX software also present in the spectra for the Ni MOFs. This suggests that some residual sulphate ions are likely present on the IDE surface, and also that another source of S contamination is likely present. Similarly, Cl is present in the $\text{HATP} \cdot 6\text{HCl}$ starting material used in the synthesis of the $\text{Cu}_3(\text{HITP})_2$ and $\text{Ni}_3(\text{HITP})_2$ MOFs, and Cl is only present in the EDX spectra for these two MOFs. Further analysis with XPS will give an insight into the chemical environments of the S and Cl, which should indicate whether it is residual starting material that is present or other contaminants.

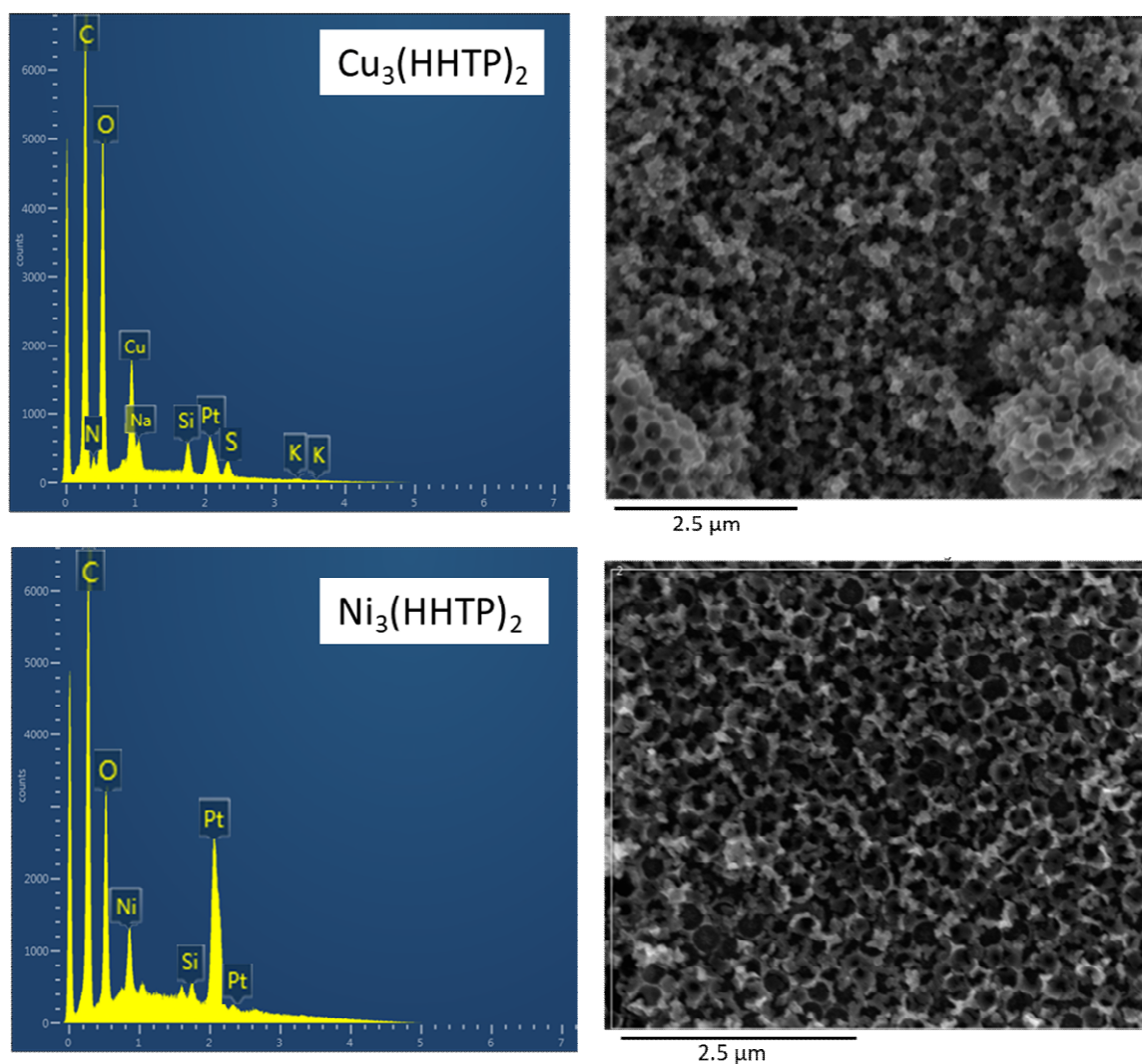


Figure 7.4: *Left* – Plots of X-ray energy in keV against counts obtained via EDX for $\text{Cu}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HHTP})_2$ samples. Both spectra show peaks with energies characteristic of the expected elemental components of the MOF, indicating that the single phase of material observed with SEM contains all of the elements known to be present in the desired MOFs. Pt, Si, Na, and N peaks originate from the substrate. The presence of S indicates that there are sulphate ions on the surface of the $\text{Cu}_3(\text{HHTP})_2$ sample. *Right* – SEM images of the areas that compositional analysis was performed on.

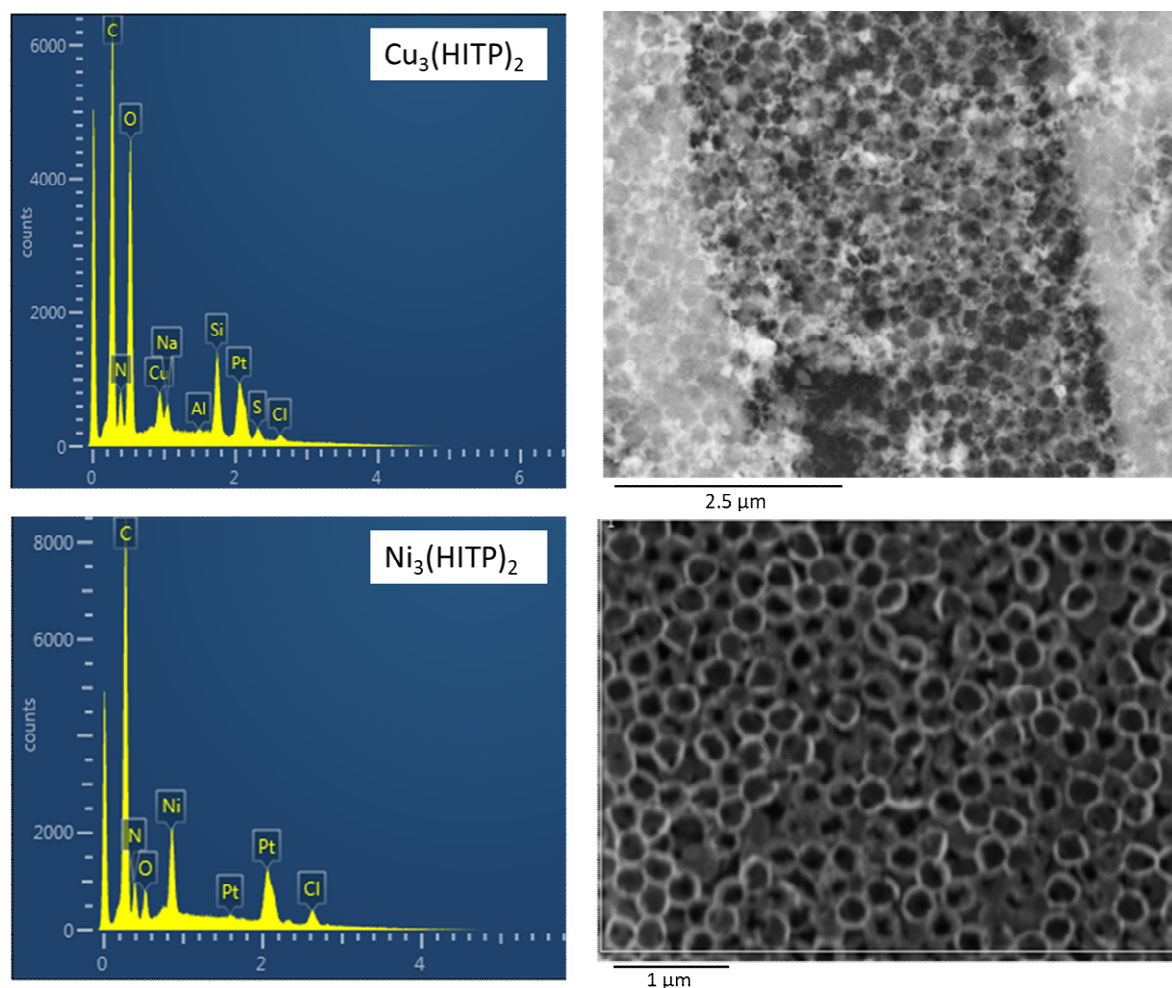


Figure 7.5: Left – Plots of X-ray energy in keV against counts obtained via EDX for $\text{Cu}_3(\text{HITP})_2$ (top) and $\text{Ni}_3(\text{HITP})_2$ samples. Both spectra show peaks with energies characteristic of the expected elemental components of the MOF, indicating that the single phase of material observed with SEM contains all of the known components of the target MOF. Pt, Si and Na peaks originate from the substrate. The presence of S indicates that there are sulphate ions on the surface of the $\text{Cu}_3(\text{HITP})_2$ sample. The presence of Cl originates from the hydrogen chloride coordinated to the ligand starting material. Right – SEM images of the areas that compositional analysis was performed on.

7.3.3 X-ray photoelectron spectroscopy

XPS was carried out on a K-alpha machine from Thermo Scientific, USA. The samples used were synthesised on IDEs as described in section 7.2 and the XPS analysis was performed without any further sample processing. An electron neutraliser was used to prevent charge build up. Figure 7.6 depicts the survey scans for the $\text{Cu}_3(\text{HHTP})_2$ and $\text{Cu}_3(\text{HITP})_2$ inverse opal samples. The $\text{Cu}_3(\text{HHTP})_2$ scan, Figure 7.6 (a), illustrates the presence of the expected elements, with a Cu 2p peak at 935.0 eV, an O 1s peak at 532.8 eV and a C 1s peak at 285.2

eV. The minor peaks present at 977.3 eV, 718.4 eV, 650.2 eV and 571.1 eV can be assigned to Cu Auger peaks, whilst the peak at 124.2 eV is consistent with the binding energy of electrons in the Cu 3s sub-shell. The peaks at 25.7 eV, 84.4 eV and 336.0 eV can be assigned to elements present in the clean IDE, as can the peak at 401.3 eV which can be assigned to the N 1s sub-shell. The small peak at 168.9 eV can be attributed to the S 2p sub-shell, indicating that some residual sulphate ions remain on the surface. The corresponding atomic % data generated by the software indicates that S only represents 1.08 % of the atoms present over the sampled area. The peak at 497.1 eV is consistent with the binding energy for a Na KLL peak, a likely component of the IDE.

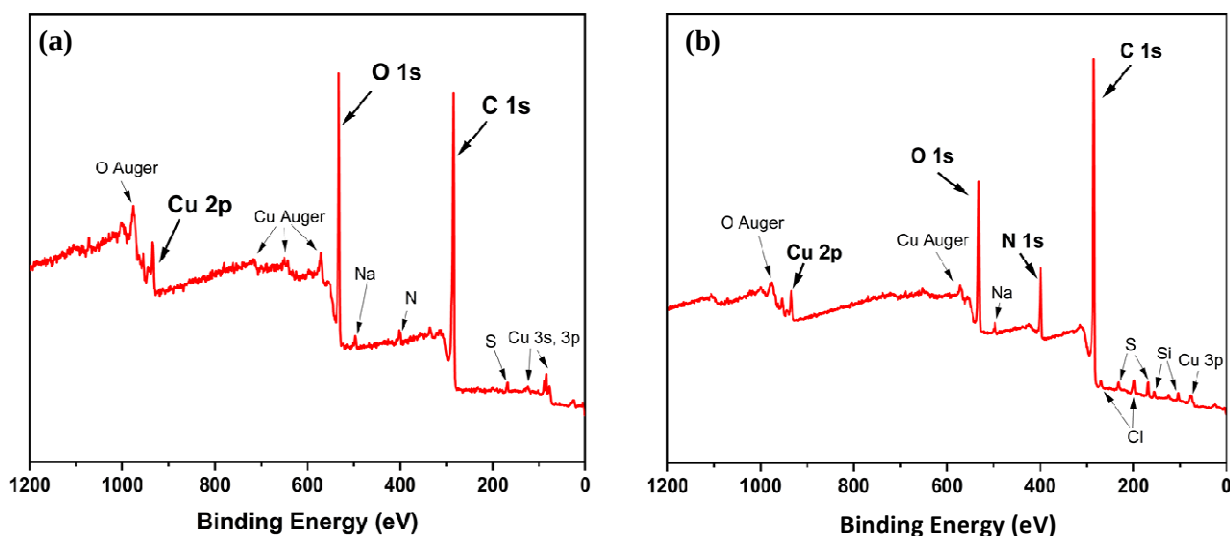


Figure 7.6: (a) XPS survey scan for the $\text{Cu}_3(\text{HHTP})_2$ MOF on glass interdigitated electrode substrate. (b) XPS survey scan for the $\text{Cu}_3(\text{HITP})_2$ MOF on glass interdigitated electrode substrate. Peaks corresponding to the Cu, C, N and O elements expected to be present in the MOF are marked in bold. S and Cl contaminant peaks are also labelled. Other peaks correspond to elements present in the IDE substrates.

Similarly, the survey scan depicted in Figure 7.6 (b) shows the presence of the known constituents of the $\text{Cu}_3(\text{HITP})_2$ MOF at 933.8 eV (Cu 2p), 399.3 eV (N 1s) and 284.9 eV (C 1s). An intense peak is also seen at 532.0 eV, corresponding to O 1s, which is present in the clean IDE. The peak at 77.4 eV can be assigned to electrons from the Cu 3p sub-shell, whilst the peaks at 26.3 eV, 104.6 eV and 154.2 eV can be assigned to electrons from elements such

as Si in the IDE, and the peak at 244.7 eV to Ar from the gas in the XPS chamber. There is some evidence for contamination with starting materials again with the peaks at 232.8 eV and 168.5 eV originating from S 2s and S 2p electrons in the metal sulphate starting material, and the peaks at 197.7 eV and 268.3 eV from the Cl 2p and Cl 2s electrons in the HATP.6HCl. Both the survey scans depicted in Figure 7.6 show the major peaks consistent with those reported for the same MOFs in literature.^{159,189} On comparing the XPS survey scans of the two Cu-based MOFs, we observe the expected increase in intensity of the N 1s peak and decrease in intensity of the O 1s peak for the HITP-MOF relative to the HHTP-MOF. This is reflective of the different elemental compositions of the MOFs with different ligands.

Higher resolution scans of the Cu 2p regions reveal further information about the chemical environment of the Cu in the two MOFs. Distinct peaks for electrons from the 2p_{3/2} sub-shells and the 2p_{1/2} sub-shells are visible for both of the Cu₃(HHTP)₂ and Cu₃(HITP)₂ samples, as labelled in Figure 7.7, which are further split into two peaks corresponding to different Cu oxidation states. As XPS peaks for neutral Cu and Cu⁺ occur at the same binding energies for copper, we cannot distinguish between the two. However, as copper ions were used as the starting material for the synthesis method described in this chapter, it is reasonable to assume that no elemental Cu is present, and as such the Cu⁺/Cu peaks will be almost entirely Cu⁺. On comparing the two spectra in Figure 7.7, it appears that a greater proportion of the Cu centres present are in the 2+ oxidation state as opposed to in their Cu⁺ form for the Cu₃(HHTP)₂ sample than for the Cu₃(HITP)₂ sample. The effect this has on the sensing performance will be discussed in section 7.4. The presence of satellite peaks in both spectra, further confirms that Cu in an oxidised state is present on the electrodes.

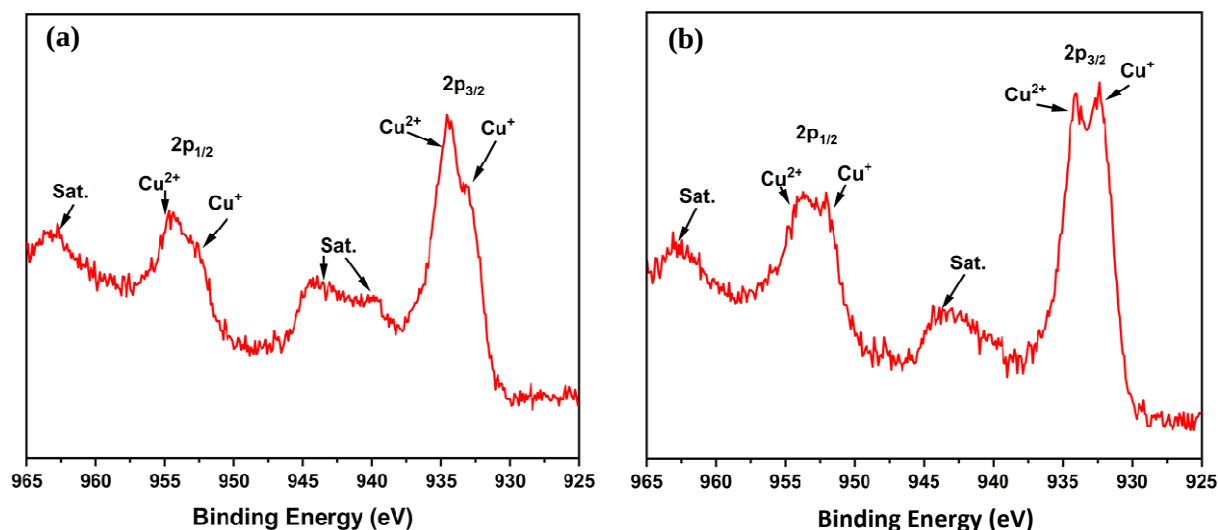


Figure 7.7: (a) High resolution XPS scan of the Cu 2p region of a $\text{Cu}_3(\text{HHTP})_2$ MOF sample on glass interdigitated electrode substrate. (b) High resolution XPS scan of the Cu 2p region of a $\text{Cu}_3(\text{HITP})_2$ MOF sample on glass interdigitated electrode substrate. Cu $2p_{3/2}$ and $2p_{1/2}$ peaks are visible in both plots, along with their associated satellites. Splitting of the $2p_{3/2}$ peak into components corresponding to Cu^+ and Cu^{2+} ions is visible for both samples, indicating that the Cu is present as a mixture of two oxidation states in the MOFs.

Survey scans of the analogous Ni-based MOFs, $\text{Ni}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HITP})_2$ also show the presence of the expected elements. For the $\text{Ni}_3(\text{HHTP})_2$ scan depicted in 7.8 (a), the expected MOF component peaks appear at 856.3 eV (Ni 2p), 532.2 (O 1s) and 284.9 (C 1s). A Ni Auger peak can also be seen at 644.5 eV, whilst oxygen Auger peaks are visible at 976.5 eV and 1001.1 eV. The peaks appearing at 398.9 eV, 154.1 eV, 103.2 eV, 71.4 eV and 24.8 eV can all be assigned to sub-shells in the N, Si and Pt components of the IDE. The peak at 168.6 eV indicates the presence of S on the IDE. This is assumed to be from environmental contamination or trace presence in the electrode substrate, as no sulphur-containing reagents were used in the synthesis of the Ni MOFs. XPS compositional analysis indicated that only 0.87 % of the sampled atoms are S.

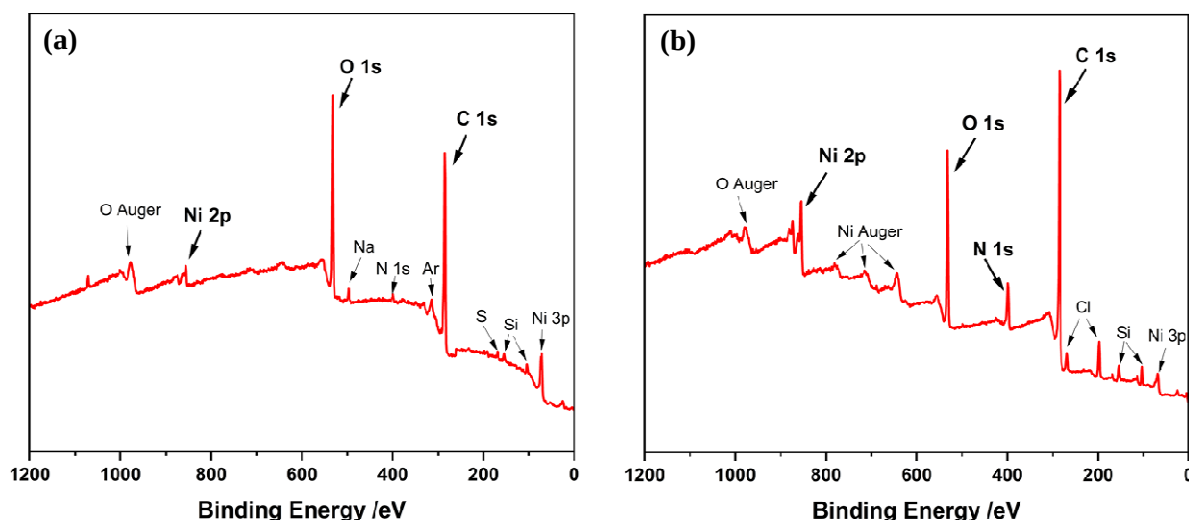


Figure 7.8: (a). XPS survey scan for the $\text{Ni}_3(\text{HHTP})_2$ MOF on glass interdigitated electrode substrate. (b) XPS survey scan for the $\text{Ni}_3(\text{HITP})_2$ MOF on glass interdigitated electrode substrate. Peaks corresponding to the MOF constituent elements, Ni, N, C and O, are marked in bold. The presence of Cl and S peaks indicate a degree of contamination.

Similarly, the survey scan of the inverse opal $\text{Ni}_3(\text{HITP})_2$ MOF sample, Figure 7.8 (b) indicates the presence of the expected constituent elements. These peaks appear at 855.5 eV (Ni 2p), 398.9 eV (N 1s) and 284.9 eV (C 1s). An intense peak at 532.1 eV can be assigned to O 1s in the IDE. An O Auger peak is visible at 978.9 eV, and Ni Auger peaks at 779.0 eV, 713.7 eV and 643.6 eV. Further Ni peaks can be seen at 69.1 eV (Ni 3p) and 113.2 eV (Ni 3s). The peaks at 103.6 eV and 154.6 eV can be assigned to Si 2p and Si 2s electrons from the IDE substrate. The peaks at 198.3 eV and 168.5 eV indicate the presence of Cl and S. Cl is present in the $\text{HATP} \cdot 6\text{HCl}$ starting material, but the origin of the sulphur contamination is unknown, as nickel acetate not sulphate was used as the Ni source. The atomic % of these are the highest of the MOFs sampled in this chapter, with 2.88 % of atoms being Cl and 3.52 % of atoms being S in the sampled area. The Cl peak at 198.3 eV is more consistent with the binding energy of a metal chloride than of organic chlorine. This is also the case for the Cl peak in the $\text{Cu}_3(\text{HITP})_2$ sample. This could imply that the Cl atoms are occupying vacant sites of the metal centres. Whether this has any noticeable effect on the sensing performance will be considered in section 7.3.4.

Higher resolution scans of the Ni 2p region can be seen in Figure 7.9. The $2p_{3/2}$ peaks occur at 855.8 eV and 855.2 eV for the HHTP and HTP samples respectively, whilst the $2p_{1/2}$ peaks appear at 873.5 eV and 872.8 eV. These values are consistent between the two samples given the error introduced by the noise in the $Ni_3(HHTP)_2$ sample. Satellite peaks at lower binding energies are visible accompanying all of the peaks in Figure 7.9. However, similar satellite peaks are present in samples of pure Ni metal, so a closer look at the binding energies is required to confirm the presence of Ni in its oxidised state. By comparing the measured binding energies of the $2p_{3/2}$ and $2p_{1/2}$ peaks with those in the ThermoFisher Elemental Database, it can be confirmed that the peaks occur at too high a binding energies for them to correspond to metallic Ni. We can therefore conclude that the Ni present is in its oxidised state. The survey scans and higher resolution Ni 2p scans are consistent with those previously reported in literature for both MOFs.^{201,139}

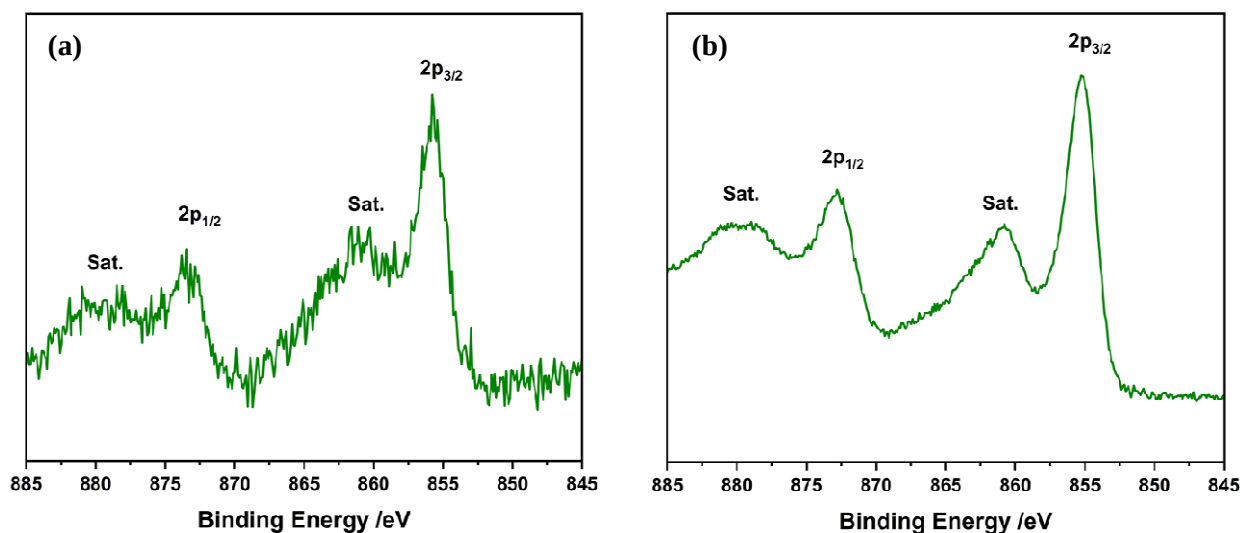


Figure 7.9: (a) High resolution XPS scan of the Ni 2p region of a $Ni_3(HHTP)_2$ MOF sample on glass interdigitated electrode substrate. (b) High resolution XPS scan of the Ni 2p region of a $Ni_3(HTP)_2$ MOF sample on glass interdigitated electrode substrate. Ni $2p_{3/2}$ and $2p_{1/2}$ peaks are visible in both plots. Their binding energies indicate that the Ni is present in its oxidised state.

The single phases of material observed via SEM, presence and even distribution of the constituent MOF elements across the inverse opal structures found by EDX, and the XPS characterisation consistent with literature reports for the known MOFs, make us confident that the method described in this chapter is successful in generating the 4 conductive MOFs.

7.4 Sensing responses

Sensors were fabricated by synthesising the 4 MOFs on the IDEs as described in section 7.2. The sensors were then placed in vials each containing 2 mL of acetone and left overnight to draw any residual solvent out of the MOF pores and activate the sensors. Sensing experiments were carried out in a specially-built chamber as described in section 3.3. The same testing conditions were used for the experiments in this chapter as those described in chapter 4. A voltage of 1 V was applied across the sensors for the tests and a dry N₂ carrier gas was used. Sensors were allowed to settle under 500 sccm of N₂ flow for at least one hour before analyte exposure commenced. Each exposure to analyte gas was 60 s in length. In the following sections the responses of the inverse opal sensors to NH₃ and NO₂ gases are reported, and conclusions about the effect of this new morphology on the sensing behaviour are drawn.

7.4.1 Sensing behaviour of Cu₃(HHTP)₂

The same Cu₃(HHTP)₂ sample that was analysed in section 7.3, with a starting resistance of around 118 Ω, was exposed to NH₃ gas with concentrations between 5 ppm and 1 ppm for 60 s. The resulting raw resistance response is depicted at the top of Figure 7.10. The plot shows reversible resistance increases on exposure to NH₃, with shapes consistent with those depicted for sensors fabricated from the same MOF via solution synthesis in section 7.2.3. The

magnitude of the sensing responses was however larger relative to the baseline drift. A baseline produced from interpolating between the points just before each analyte exposure was subtracted from the data to obtain the plot depicted in the centre of Figure 7.10. The corresponding calibration plot can be seen at the bottom of Figure 7.10. The gradient of the best fit line in this plot equates to the sensitivity of the sensor; $0.097 \pm 0.008 \text{ \% ppm}^{-1}$. The limit of detection calculated from this sensitivity is $0.31 \pm 0.03 \text{ ppm}$, putting the LOD between that of the solution-synthesised α -Cu₃(HHTP)₂ and n -Cu₃(HHTP)₂ samples discussed in chapter 4.

The fact that the same response shape is observed suggests that the sensing mechanism discussed in section 4.4 still applies, and that the introduction of the hierarchical porosity by way of the inverse opal morphology, has not impacted the sites of the Cu₃(HHTP)₂ and NH₃ gas interaction. We therefore assume that the NH₃ gas interacts with the Cu metal centre through a combination of direct interaction with the Cu metal, and by interacting with H₂O coordinated to the Cu centres, as described in section 4.4. Both of these effects result in donation of electron density to the framework, reducing the concentration of holes and so increasing the resistance. By Rubio-Giménez et al.'s conclusions, this would also distort the planarity at the metal centres,¹⁴⁴ pushing the layers apart slightly and disrupting the through-space charge transport pathway.

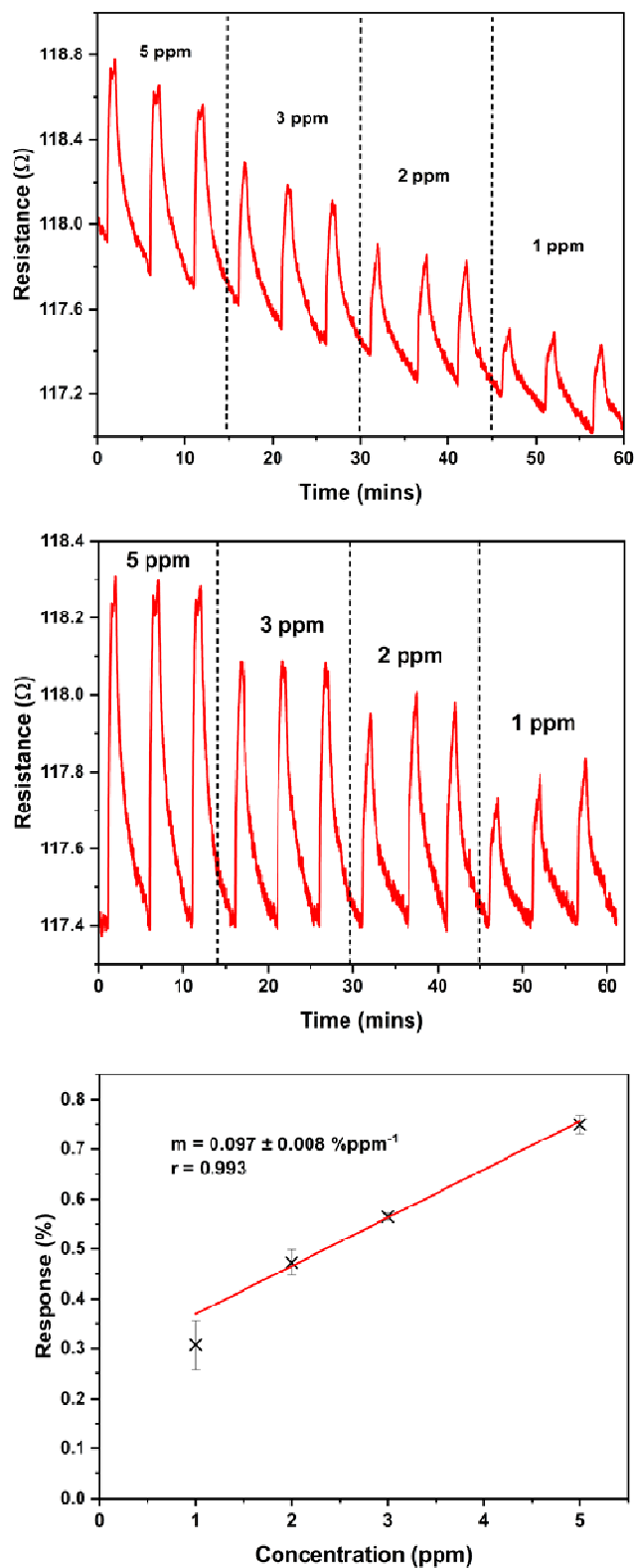


Figure 7.10: Top - Resistance change of a $\text{Cu}_3(\text{HHTP})_2$ sensor with inverse opal morphology exposed to NH_3 gas with concentrations between 5 and 1 ppm. Reversible increases in resistance are observed. **Centre** - Baseline corrected resistance change of the sensor exposed to NH_3 gas. **Bottom** - Corresponding calibration plot for the response to NH_3 .

Whilst the LOD of this hierarchically porous sample is superior to that of the sensor made from solution-synthesised rod-shaped crystals, *a*-Cu₃(HHTP)₂, it is less good than that made from a similar sensor of flake-like *n*-Cu₃(HHTP)₂ crystals. However, it should be noted that the sensing performance of the sensors fabricated in chapter 4 cannot be directly compared with those here, as the mass of MOF present for each sensor will not be the same. In chapter 4, 30 × 5 µL drops of 10 mg mL⁻¹ MOF solution are deposited onto the electrodes, resulting in an estimated 1.5 mg of MOF on each electrode. In this chapter however, if the yield of the reaction were 100 %, only 0.22 mg of MOF could be present on each electrode. Performing the same synthesis as described in section 7.2, but substituting the ligand and nanosphere solution for a solution of just the ligand does not result in MOF formation, and so a comparison cannot be drawn there either. Given the low mass of MOF on the electrodes from this templated synthesis method, we consider the LOD calculated here to be good.

The observed response of the same hierarchically porous Cu₃(HHTP)₂ sensor to NO₂ gas was also largely consistent with that of the analogous solution-synthesised MOF sensor. The raw resistance plot in Figure 7.11 depicts an irreversible resistance decrease on exposure to NO₂. We therefore anticipate that the same permanent binding of the NO₂ to the pendant oxygen lone pairs on the ligand is responsible for this change (section 4.4). The percentage change in resistance on exposure to 5 ppm of NO₂ is lower than those of the solution synthesised samples, at 2.3 % compared to the 19.6 % and 8.7 % responses for the *a*-Cu₃(HHTP)₂ and *n*-Cu₃(HHTP)₂ samples respectively.

There is however a small initial increase on exposure of the sensor to 5 ppm of NO₂. As this is only visible for the 5 ppm exposure, we assume this response to be an effect of the temporary change in pressure when the gas flow is changed to introduce the analyte, and is therefore an artefact of the test. As a 10 ppm NH₃ cylinder is used, a 5 ppm exposure is made from mixing

250 sccm of N₂ carrier with 250 sccm of gas flow from the 10 ppm NH₃ cylinder. This means that on transferring from the pure N₂ flow to the 5 ppm NH₃ flow, the flow from one cylinder is dropped by 50 % and the other increased from 0 to 250 sccm. Any delay in changing the flow of one cylinder could therefore induce a short-lived change in pressure of the air flowing across the sensor. Such spikes were observed in control experiments when the relative flow rates of two identical N₂ gas flow lines were changed. They are more common for the first exposure of a sensor but decrease in intensity rapidly with subsequent exposures. They can be distinguished from genuine sensing responses as their resistances start to recover within 20 s of the analyte exposure starting.

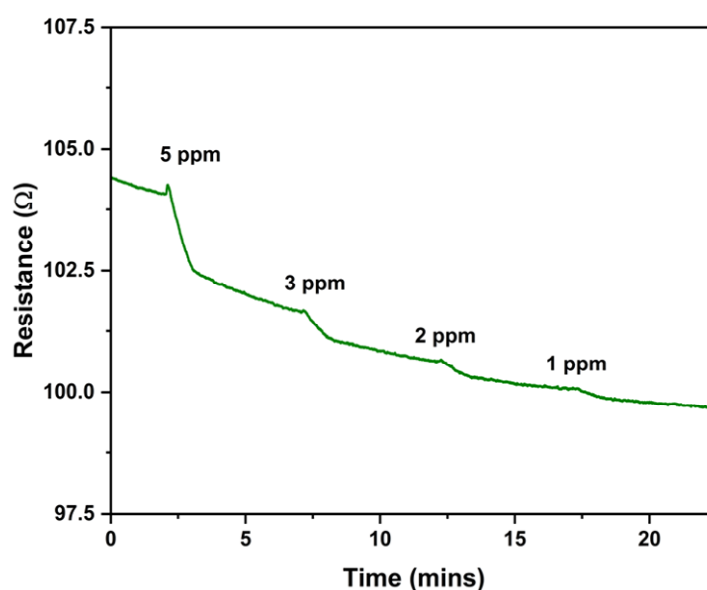


Figure 7.11: Resistance change of a Cu₃(HHTP)₂ sensor with inverse opal morphology exposed to NO₂ gas with concentrations between 5 and 1 ppm. Irreversible resistance decreases are observed. The small increase in resistance observed at the start of the 5 ppm exposure is assumed to be an artefact of the gas sensing set-up.

7.4.2 Sensing behaviour of $\text{Cu}_3(\text{HITP})_2$

The $\text{Cu}_3(\text{HITP})_2$ sensor fabricated from a polystyrene nanosphere template responded differently to NH_3 gas when compared to the solution-synthesised $\text{Cu}_3(\text{HITP})_2$ sensors. Figure 7.12 shows the response of the template-synthesised MOF to NH_3 gas with concentrations between 5 and 1 ppm. Instead of showing the reversible resistance increases on exposure to NH_3 like the solution-synthesised samples, Figure 7.12 shows an initial reversible resistance increase which is then taken over by an irreversible resistance decrease. This multi-component response implies that the NH_3 is interacting with the framework in more than one way. The initial resistance increase is likely to be due to NH_3 interacting with the framework via the same mechanism described in section 4.4, at vacant sites on the Cu above and below the MOF conjugation plane, decreasing the charge carrier concentration and increasing the resistance.

The second contribution to the sensing response could be rationalised by considering the presence of Cl as detected via XPS and EDX. The rapid nature of this synthesis method, and the fact that the ligand and metal salt are only present in solution simultaneously for a very short period of time, makes it likely that the HCl from the HATP.6HCl ligand will remain in the vicinity of the MOF during the MOF formation reaction, as opposed to being dissolved into the solution and reacting with the added base as we would anticipate to occur during conventional solution synthesis. The XPS data indicated that the Cl present was in the form of a metal chloride, and therefore likely bonded to the Cu centre directly. It could be then that the irreversible component of the response comes from NH_3 interacting with the Cl-containing species bonded to the Cu, rather than with the Cu directly. HCl molecules would coordinate to the Cu centre via the Cl, which donates electron density to the Cu. Incoming NH_3 could then react with the HCl coordinated to the MOF to form ammonium chloride, NH_4Cl . If the NH_4Cl then detaches from the MOF, the electron donating effects of the Cl-containing

molecule would be removed. The concentration of holes in the MOF would therefore increase and the resistance would decrease. NH_4Cl re-coordinating to the metal centre would be unlikely, making this an irreversible resistance change. The shape of the response indicates that the resistance increase due to NH_3 occupying vacant Cu sites dominates early in the gas exposure, but once all of the vacant metal sites have been occupied by NH_3 , interaction of the NH_3 via HCl already interacting with the metal will have the dominant effect on the resistance.

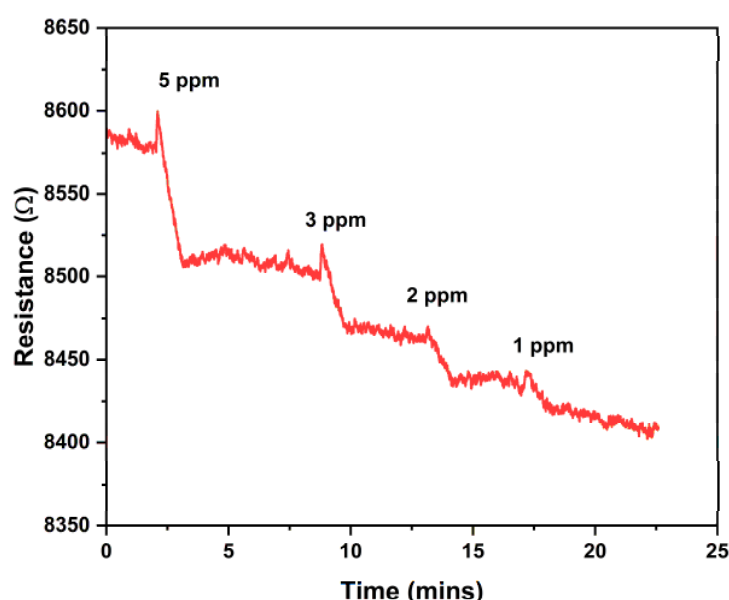


Figure 7.12: Resistance change of a $\text{Cu}_3(\text{HITP})_2$ sensor with inverse opal morphology exposed to NH_3 gas with concentrations between 5 and 1 ppm. The responses show an initial reversible increase in resistance followed by an irreversible resistance decrease. It is suspected that HCl occupying vacant sites on the metal is responsible for the irreversible component of the response.

When exposed to NO_2 gas, the same inverse opal $\text{Cu}_3(\text{HITP})_2$ sensor showed no resistance response. This is in contrast to the analogous sensor made from solution synthesised $\text{Cu}_3(\text{HITP})_2$ which showed reversible resistance increases when exposed to NO_2 . In section 4.4, this reversible increase was attributed to interaction of the NO_2 at the Cu metal centre, enabled by the redox communication between the ligand and the metal. The reason for the absence of such a response for the inverse opal structure is unclear, but it is likely that coordinated HCl is impacting the approach of the NO_2 to the metal centre.

7.4.3 Sensing behaviour of $\text{Ni}_3(\text{HHTP})_2$

The $\text{Ni}_3(\text{HHTP})_2$ sensor visible at the bottom of Figure 7.2 was found to respond to NH_3 gas with reversible resistance increases, Figure 7.13. In contrast, sensors fabricated from the same MOF synthesised via solution synthesis showed no resistance change on exposure to NH_3 (section 4.2.3). Whilst the magnitude of resistance change was not sufficiently linearly related to the analyte concentration for an LOD to be calculated, the presence of any resistance response presents a step toward increasing the applications of this MOF.

When exposed to NO_2 gas, the same sensor made from templated synthesis responded with similar irreversible resistance decreases to those observed for the analogous solution-synthesised sensor. The results of this experiment can be seen in Figure 7.14. The percentage change in resistance when exposed to 5 ppm of NO_2 was 17.4 %, similar to the 17.0 % recorded for the solution-synthesised sensor. This implies that the same permanent binding of NO_2 to the pendant lone pairs on oxygen atoms present in the ligand (section 4.4) dominates for both the solution-synthesised and templated MOF sensors.

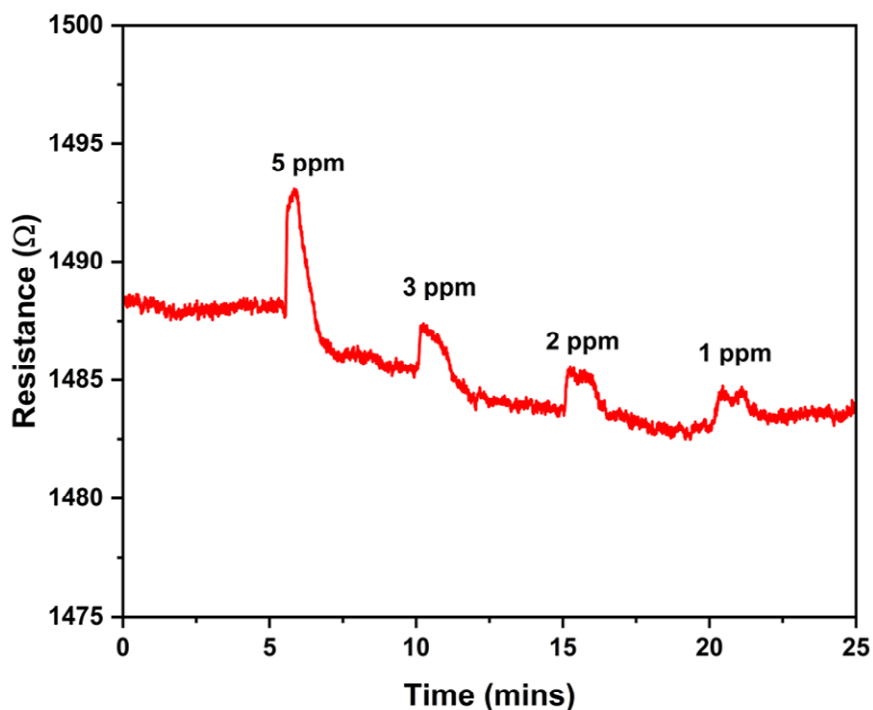


Figure 7.13: Resistance change of a $\text{Ni}_3(\text{HHTP})_2$ sensor with inverse opal morphology exposed to NH_3 gas with concentrations between 5 and 1 ppm. Unlike the analogous solution-synthesised $\text{Ni}_3(\text{HHTP})_2$ MOF sensor, this inverse opal sensor shows reversible resistance increases on exposure to NH_3 .

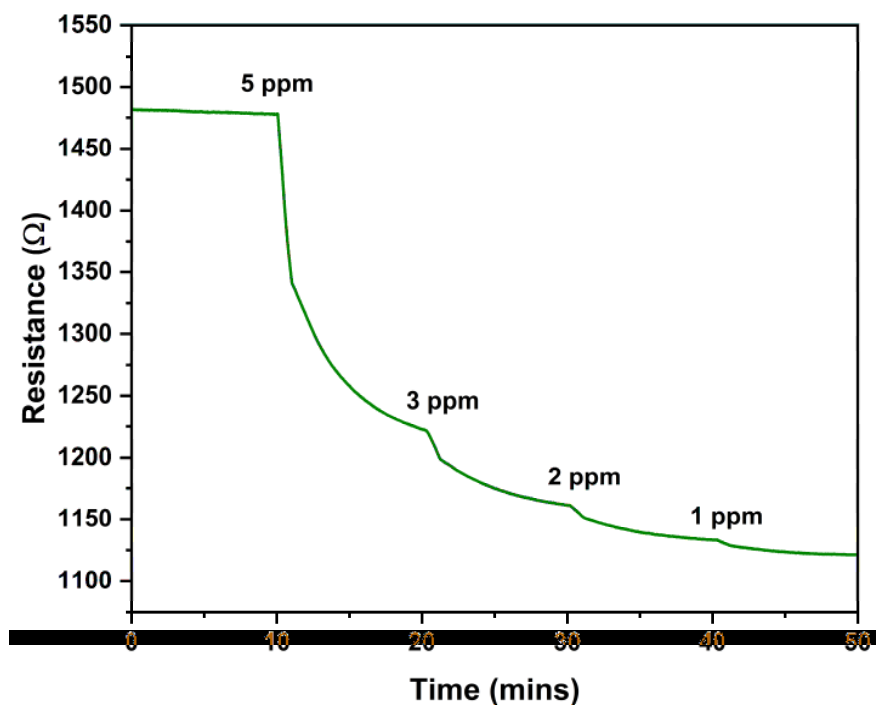


Figure 7.14: Resistance change of a $\text{Ni}_3(\text{HHTP})_2$ sensor with inverse opal morphology exposed to NO_2 gas with concentrations between 5 and 1 ppm. Irreversible resistance decreases are observed on exposure to NO_2 .

A new sensing mechanism is required to rationalise how the NH_3 interacts with the inverse opal $\text{Ni}_3(\text{HHTP})_2$ to give reversible resistance increases, whilst no response is seen when the same gas interacts with solution-synthesised $\text{Ni}_3(\text{HHTP})_2$. Differences between the MOFs synthesised from the two methods could arise from the limited time the reactants spend in solution, difference in pH of the reaction mixtures, or differences in the resulting MOF morphologies. For the Ni MOFs it is known that no Ni^+ ions are present, only Ni^{2+} ions. This means that at any defects or capping points of the layers where the metal centres cannot bond to enough anionic ligand groups, OH^- ions are likely to coordinate to the Ni^{2+} centres to maintain charge neutrality. Of the four MOFs focused on in this thesis, $\text{Ni}_3(\text{HHTP})_2$ is likely to contain the most M—OH groups due to its interpolated structure, whereby every other layer is comprised of discrete Ni_3HHTP units. Each of the three Ni centres in the Ni_3HHTP units must be coordinated to an OH^- ion for charge balance. The rapid nature of the templated synthesis described in this chapter is likely to introduce more defects than in the slower solution synthesis growth method, and so it is anticipated that there is a higher concentration of M—OH groups in the templated sample. These OH^- groups will be more resistant to removal by acetone than coordinated H_2O molecules and so are likely still present during the sensing experiments. The OH^- groups donate electron density to the Ni^{2+} centres. When the sample is exposed to NH_3 , the NH_3 can donate electron density to the H of the OH^- group, in turn allowing the OH^- group to donate more electron density to the MOF. This results in a reduction in the hole concentration and an increase in resistance of the p-type semiconducting MOF.

7.4.4 Sensing behaviour of Ni₃(HITP)₂

The Ni₃(HITP)₂ MOF synthesised with an inverse opal structure showed no resistance responses on exposure to either NO₂ or NH₃ analytes, consistent with the behaviour of solution-synthesised Ni₃(HITP)₂. The lack of response to NO₂ analyte can again be rationalised by the lack of pendant lone pairs in the conjugation plane (see section 4.4). The lack of NH₃ interaction was rationalised for the solution-synthesised sample in terms of the absence for evidence for redox communication between the ligand and metal, and lack of flexibility in stable oxidation states of Ni. However, in the case of the inverse opal Ni₃(HHTP)₂ MOF, a response to NH₃ was seen. This was attributed to the suspected presence of M—OH groups at defects. The concentration of these groups is likely to be less for the Ni₃(HITP)₂ MOF due to its slipped parallel structure, as opposed to the interpolated structure of Ni₃(HHTP)₂. It could also be reasonable to assume that the presence of the HCl molecules in the reaction mixture as part of the HATP.6HCl reactant for the HITP MOF synthesis may act to reduce the alkalinity of the solution, increasing the proportion of H₂O ligands relative to OH ligands and so reducing this effect for the analogous HITP-based MOF. This would result in a lower concentration of Ni—OH moieties in the Ni₃(HITP)₂ sample compared to the Ni₃(HHTP)₂ sample, resulting in a diminished resistance response to NH₃.

7.5 Conclusion

Cu₃(HHTP)₂, Cu₃(HITP)₂, Ni₃(HHTP)₂ and Ni₃(HITP)₂ MOFs have all been synthesised with inverse opal morphologies via templated synthesis around polystyrene nanospheres. The samples were analysed using SEM, EDX and XPS. Following on from the experiments performed in section 4.2, where the morphology of Cu₃(HHTP)₂ was found to have a significant effect on the sensing performance, the sensing behaviour of these inverse-opal

structured MOFs were analysed. The templated $\text{Cu}_3(\text{HHTP})_2$ sample showed the same sensing response shape when exposed to both NH_3 and NO_2 analyte gases as the analogous solution synthesised samples. The LOD for NH_3 gas was 0.31 ± 0.03 ppm, which is between the LODs of the solution-synthesised $\alpha\text{-Cu}_3(\text{HHTP})_2$ and $n\text{-Cu}_3(\text{HHTP})_2$ samples discussed in chapter 4. From this we conclude that the same sensing mechanisms are taking place, and that the inverse opal morphology offers an advantage in terms of LOD relative to the rod-like $\text{Cu}_3(\text{HHTP})_2$ crystals, but not compared to the flake-like crystals. However, the response magnitude of the template-synthesised MOF sensor is considered good considering the small mass of MOF present on the electrodes. It is likely that the macropores introduced by the nanosphere template aid access to the micropores in the MOF structure.

The templated $\text{Cu}_3(\text{HITP})_2$ MOF showed a multicomponent sensing response when exposed to NH_3 , with evidence of both a reversible resistance increase and irreversible resistance decrease. This irreversible component was not observed for the solution-synthesised MOF sensor. Furthermore, the templated MOF did not respond to NO_2 whilst the solution synthesised MOF did. These differences were attributed not to the change in morphology, but to the inclusion of Cl in the MOF as a result of the quasi solid-liquid synthetic method used for the templated synthesis. The $\text{Ni}_3(\text{HHTP})_2$ templated MOF sample also showed differences to its solution synthesised counterpart, with reversible increases in resistance observed when the templated MOF was exposed to NH_3 , whereas no response was registered for the solution synthesised MOF. The findings of this experiment suggests that the response of the MOF can be manipulated by changing the reaction conditions. Whilst the role of the inverse opal morphology on the sensing behaviour alone could not be decoupled from the other effects of using this synthesis method, we anticipate the inverse opal structure to be of interest to those working on MOF-based capacitors, or other devices where diffusion and pore accessibility

dictate their performance. We anticipate the next step of this work to be on moving away from drop-casting techniques whilst retaining the inverse opal morphology, enabling larger scale areas to be coated in the MOF. This would enable PXRD data to be obtained, and for any permanent impact on the interlayer separation by the analyte to be explored.

Chapter 8

Summary and future outlook

This final chapter begins with a summary of the scientific progress made during this project. This is followed by a discussion of the implications of the results, which then leads on to a broader look at the future of chemiresistive MOF gas sensors and finally a discussion of some of the preliminary work undertaken to further the research described in this thesis.

8.1 Scientific progress

In this thesis two routes to synthesise uniform distributions of conductive MOFs in situ on different substrates have been developed. Additionally, sensors have been fabricated from solution-synthesised conductive MOFs, electrochemically synthesised MOF, and hierarchically porous MOF structures. Comparing their sensing performances has given us additional insight into the sensing mechanisms responsible.

Solution-synthesised MOF sensors: Structurally analogous $\text{Cu}_3(\text{HHTP})_2$, $\text{Cu}_3(\text{HITP})_2$, $\text{Ni}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HITP})_2$ MOFs were synthesised using known solvothermal methods. Sensors were fabricated from them by drop-casting ethanolic suspensions of the MOF powders onto IDEs. Their sensing responses to NH_3 and NO_2 gases were then probed. To our knowledge, a systematic study that fabricates these 4 MOFs and tests their sensing responses in a way that means they can be meaningfully compared has not been reported. By analysing the sensing responses of the different MOFs alongside each other, we were able to conclude that the HHTP linker is the site of interaction with NO_2 gas, something that has not been

reported before. Our experiments supported conclusions about the sensing mechanism responsible for NH_3 sensing, and also confirmed that particle morphology has a significant effect on the sensing performance of $\text{Cu}_3(\text{HHTP})_2$ NH_3 sensors.

Synthesis of conductive MOFs from metal nanoclusters: By pre-patterning fabric, paper, glass IDE and Au substrates with Cu and Ni nanoclusters deposited from a magnetron sputtering source, uniform distributions of $\text{Cu}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HHTP})_2$ MOFs were formed in situ on the substrates. The nanoclusters acted as the sole source of Cu or Ni metal for the MOF synthesis, and the desired MOFs grew anchored to the substrates. For applications of conductive MOFs such as chemiresistive sensing, it is necessary for the MOF to be adhered to insulating substrates, or bridging insulating gaps between conductive electrodes. This method was successful on all of the substrates attempted, including insulating and flexible ones. We therefore anticipate this method to be useful to those looking to integrate MOFs as active components in flexible and wearable electronic devices such as chemiresistive sensing textiles.

Electrochemical growth of a conductive MOF from metal nanoclusters: A method to electrochemically grow $\text{Cu}_3(\text{HHTP})_2$ MOF from Cu nanoclusters deposited on Pt/glass IDEs has been developed. This method enables the advantages of electrochemical growth techniques to be combined with the advantages of the nanocluster MOF growth method described above. The conductive MOF is fabricated in situ on the IDEs required for sensing, removing the need to remove the MOF from a bulk metal electrode and re-adhere it to the desired IDEs. The distribution of MOF reflects the even distribution of the Cu nanoclusters, and the MOF is formed strongly adhered to the IDE. Some of the high contact resistance MOF-MOF particle boundaries are replaced by nanocluster-MOF boundaries, and MOF only grows from nanoclusters electrically connected to the electrodes. A representative sensor

fabricated using this method required no baseline correction and was able to detect NH_3 gas with a calculated LOD of 0.158 ± 0.006 ppm, making it a superior sensor to most metal oxide semiconductors which typically report LODs in the region of 2 – 5 ppm.⁷ This method is anticipated to be highly useful for those looking to grow $\text{Cu}_3(\text{HHTP})_2$ MOF in a controlled manner for incorporation into a variety of electronic devices, and to reliably and quickly fabricate chemiresistive sensors.

Fabrication of MOF sensors with inverse opal structures: The work performed by Miao et al.¹⁹⁰ was expanded upon to form inverse opal structures of $\text{Cu}_3(\text{HHTP})_2$, $\text{Ni}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HITP})_2$ MOFs in addition to the $\text{Cu}_3(\text{HITP})_2$ that they report synthesising. Aside from developing the method to synthesise additional MOFs, these hierarchically porous structures were used to fabricate sensors. The sensing responses to NH_3 and NO_2 gases were explored, and it was found that the $\text{Ni}_3(\text{HHTP})_2$ MOF sensor made from the MOF with an inverse opal structure showed evidence of a reversible resistance response to NH_3 , whilst no response was observed for an analogous sensor made from the same MOF synthesised via conventional methods. This difference was rationalised in terms of the alkalinity of the solution used in the synthesis, combined with the effects of the nanosphere template. In addition, a sensor made from hierarchically porous $\text{Cu}_3(\text{HITP})_2$ MOF gave a sensing response with both reversible resistance increase and irreversible resistance decrease components on exposure to NH_3 . This is different to the pure reversible resistance increase exhibited with the conventionally synthesised $\text{Cu}_3(\text{HITP})_2$ sensor. This difference was attributed to the inclusion of Cl in the MOF framework, a side-effect of the rapid synthesis method used to create the inverse opal structures. This work has provided an insight into the role of dopants such as Cl, solution pH and morphology on the sensing behaviour of these MOFs. These insights suggest that it may be possible to tailor the reversibility and response types of conductive MOFs to particular

analytes through changing the morphology and solution conditions. In the longer term this would provide the potential for highly selective arrays of MOFs to be formed, in which each array component is comprised of a sensor made of the same MOF, but synthesised in a different way.

8.2 Implications of the research

In general, the results described in this thesis are anticipated to play an important role in accelerating the development of real-world devices containing conductive MOFs. In chapter 4, the identification of the oxygen on the ligand as the likely site for interaction with NO₂ is important for directing the design of future MOFs for NO₂ sensing. Studies of the sensing responses of the same MOFs synthesised with inverse opal structures in chapter 8, demonstrated that changing the synthesis method could result in changes in the MOF that mean they can function as sensors even when the same MOF made from traditional methods cannot. This finding can inform future work to design strategies for making MOFs that give the desired sensing responses. Moreover, the macroporous arrangement of the microporous MOF, induced by the nanosphere template, is of potential benefit to those looking to use MOFs in applications where regular arrangements of accessible pores are required. To this end, the use of such MOF structures in gas storage or capacitors could yield interesting results.

The method of synthesising Cu₃(HITP)₂ and Ni₃(HITP)₂ MOFs in situ on a variety of substrates, chapter 5, is expected to be of wide applicability. The demonstrated success in synthesising conductive MOFs on flexible and insulating substrates in particular, could be used in applications such as wearable toxic gas sensors for industrial or military applications.

The gas sensor made from $\text{Cu}_3(\text{HHTP})_2$ that was electrochemically grown from pre-patterned Cu nanoclusters, had a superior limit of detection to the majority of metal oxide semiconductor gas sensors, the current industry standard.⁷ In addition, this LOD was achieved at room temperature. This method offers advantages over other MOF synthesis methods in that it does not require a metal salt, it generates MOF with a uniform distribution, it circumvents the need to remove the MOF from a conductive substrate and re-adhere it to an insulating one, no gas bubbling through the solution is required, and the MOF is generated in situ on and strongly adhered to the substrate. The method is a reliable way of generating chemiresistive NH_3 sensors, and could therefore find a use in exhaled breath diagnostic devices. NH_3 gas is known to be present at elevated levels in the exhaled breath of persons with helicobacter pylori infections, so the sensor fabricated in chapter 6 could be applied in an application like this. Moreover, the methods of MOF synthesis described in both chapters 5 and 6 could be further employed in applications beyond chemiresistive gas sensing. Ways of generating uniform distributions of conductive MOFs in situ on the desired substrates are required by those looking to make MOF-based supercapacitors, electrodes for batteries and electrocatalysts.

In comparison to NH_3 gas sensors made from alternative sensing media, the limits of detection calculated for all of the sensors in this thesis are competitive.⁷ The current favoured NH_3 sensors are based on metal oxide semiconductors, most of which report LODs between 2 and 5 ppm. The LOD of 0.158 ppm for our electrochemically synthesised sensor was only outperformed by the $\text{SnO}_2/\text{In}_2\text{O}_3$ sensor fabricated by Qi et al. who quote a 0.100 ppm LOD.²⁰² The sensors described in chapters 4 and 7 all have LODs between 0.12 and 1.2 ppb which means that they too are competitive with metal oxide semiconductors. Conducting polymer, field effect transistor, electrochemical and surface acoustic wave sensors typically quote LODs of a similar magnitude to those of metal oxide semiconductors, making the sensors

described in this thesis competitive with these devices also.⁷ Tunable diode laser absorption spectrometry sensors are able to detect NH_3 at lower concentrations (the lowest quotes an LOD of 6 ppb²⁰³) but are disadvantaged by their cost, complexity and size.

8.3 Broader outlook

The reported work on conductive MOFs in this thesis and the wider literature is very promising but further progress needs to be made before chemiresistive gas sensors can be used in real-world devices. Specifically, their tolerance to ambient humidity and other chemicals in the air needs to be explored more thoroughly. Experiments on the response of MOF sensors to mixtures of gases have been reported, but are not yet reflective of likely atmospheric conditions in real-life situations such as airports, venues and hospitals. To make sensors that are selective for the desired analyte gas, and that do not register false positives to other environmental contaminants, chemiresistive sensing arrays can be made. Prototypes of such arrays have been made from MOF sensors such as the 3-component array made by Campbell et al.¹⁵² and the 4-component array fabricated by Ko et al..¹⁵³ To achieve reliable selectivity for use in real-world environments, the MOFs need to be tailored very specifically to only interact with the desired analyte, or higher component arrays need to be fabricated. Such arrays could involve MOF sensor components as well as components based on other chemiresistive sensing media such as conducting polymers or metal oxide semiconductors.

Should these issues be overcome, MOF-based chemiresistive gas sensors could be utilised in a multitude of ways. For example, both NH_3 and NO_2 gases can be present at elevated levels in the vicinity of improvised explosive devices made from substances such as fertilisers.²⁰⁴ Such sensors may therefore have a place in the explosives detection industry, for use in

settings such as airports or landmine detection. Integration of the sensors with the Internet of Things, IoT, would enable data from a number of sensors in different locations to be collected and processed together, to trigger alarms or control safety systems.²⁰⁵ Sniffer dogs are currently the gold standard for work in this area, but the expense and time associated with training and handling them has driven a demand for a technological solution. Moreover, chemiresistive sensors for volatile organic compounds could be integrated into fridges to alert us when the contents is off, or into smart watches that you can breathe onto to get data about your current metabolic rate indicated by acetone levels. The progress described in this thesis takes us a step closer to being able to manufacture such devices.

Future and current technological advancements are likely to accelerate progress further. For example, advances in machine learning techniques can be used to improve the accuracy of conclusions made from sensor array data, and generative artificial intelligence may soon be able to predict the structures of MOFs that will interact best with particular analytes.

8.4 Future work

To build directly on the findings reported in this thesis, a number of preliminary experiments have been performed, many of which have shown promising results. Success has been had in synthesising a conductive MOF with Fe metal centres, $\text{Fe}_3(\text{HHTP})_2$ and initial sensing experiments suggest that it responds to NH_3 gas. As Fe can exist in multiple stable oxidation states, it could be that this MOF responds differently to a number of analytes, which could make it a valuable component of a selective chemiresistive sensing array.

There is also scope to further optimise the conductive MOF sensors described in chapters 6 and 7. For the hierarchically porous MOF structures described in chapter 7 for example,

nanospheres of different sizes could be used as the template, and the effect of the different mesopore dimensions on the sensing responses could be studied.

For the electrochemically synthesised samples described in chapter 6, it is anticipated that sensors with the highest sensitivity and best LODs will be fabricated when a percolation network of MOF exists bridging the insulating IDE gaps. For a system comprised of a random mixture of insulating and conductive components, below a certain concentration of conductive material the system is insulating. As the amount of conductive material is increased, discrete areas within which current could flow grow until enough of these regions connect to form a continuous path for current to flow across the system, this is the percolation threshold and the system is no longer insulating. For the case of depositing conductive material such as MOF randomly across an insulating gap between two electrodes, we do not see a step change from insulator to good conductor, but a region in which the conductivity rapidly changes with amount of conductive material. This region is referred to as the percolation region and is the region in which the measured resistance changes the most for a given change in amount of conductive material. This means that sensors made from percolation networks should give the greatest percentage responses on exposure to analytes, as disruption to small numbers of conductive pathways due to analyte interactions have the most significant effect on the measured resistance. Percolation networks of conducting polymers have been found to be more sensitive gas sensors than thick films,²⁰⁶ and initial experiments suggest this will be the case for MOF sensors too. MOF sensors at different points on the percolation curve can be fabricated by changing the electrochemical synthesis time, and the real-time sensor resistance has been measured as the MOF grows using the same method as that described by Li et al. in 2022.²⁰⁶ Completion of these experiments is expected to show a clear minimum in limit of

detection corresponding to electrochemically synthesised $\text{Cu}_3(\text{HHTP})_2$ sensors operating in the percolation region.

As part of this project, percolation networks containing MOFs were also fabricated by mixing Ag nanowires with conductive MOF powders in different ratios and drop-casting the solution onto paper. Pressing the paper after deposition with a mechanical press was found to improve the conductivity. Effective NH_3 and NO_2 sensors were fabricated using this method but more experiments are required to optimise the ratio of MOFs to Ag NWs and exploit the phenomenon of electrical percolation for sensitivity benefit. Furthering these investigations could be a promising route to easily fabricate highly sensitive gas sensors on paper substrates.

I anticipate that continuing with these experiments will yield significant results that will further shape work in this area, and help to bring MOF-based chemiresistive gas sensors closer to use in real-world devices.

References

- 1 Markets and Markets, Gas Sensors Market Size, Share and Industry Growth Analysis Report, Forecast to 2028, 2023, Report Code: SE 4323.
- 2 E. H. M. Camara, P. Breuil, D. Briand, N. F. de Rooij and C. Pijolat, A micro gas preconcentrator with improved performance for pollution monitoring and explosives detection, *Anal. Chim. Acta*, 2011, **688**, 175–182.
- 3 M. Leidinger, M. Rieger, D. Weishaupt, T. Sauerwald, M. Nägele, J. Hürttlen and A. Schütze, Trace gas VOC detection using metal-organic frameworks as preconcentrators and semiconductor gas sensors, *Procedia Eng.*, 2015, **120**, 1042–1045.
- 4 A. Rescalli, D. Marzorati, S. Gelosa, F. Cellesi and P. Cerveri, Temperature Modulation of MOS Sensors for Enhanced Detection of Volatile Organic Compounds, *Chemosensors*, 2023, **11**, 1–16.
- 5 S. W. Chiu and K. T. Tang, Towards a chemiresistive sensor-integrated electronic nose: A review, *Sensors*, 2013, **13**, 14214–14247.
- 6 S. Kitagawa, R. Kitaura and S. Noro, Functional Porous Coordination Polymers, *Angew. Chemie Int. Ed.*, 2004, **43**, 2334–2375.
- 7 D. Kwak, Y. Lei and R. Maric, Ammonia gas sensors: A comprehensive review, *Talanta*, 2019, 713–730.
- 8 E.-X. Chen, H. Yang and J. Zhang, Zeolitic Imidazolate Framework as Formaldehyde Gas Sensor, *Inorg. Chem*, 2014, **53**, 5411–5413.
- 9 O. M. Yaghi and H. Li, Hydrothermal Synthesis of a Metal-Organic Framework Containing Large Rectangular Channels, *J. Am. Chem. Soc.*, 1995, **117**, 10401–10402.
- 10 H. Furukawa, K. E. Cordova, M. O’Keeffe and O. M. Yaghi, The chemistry and applications of metal-organic frameworks, *Science*, 2013, **341**, 1230444.
- 11 O. M. Yaghi, M. O’Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, Reticular synthesis and the design of new materials, *Nature*, 2003, **423**, 705–714.
- 12 C. Singh, S. Mukhopadhyay and I. Hod, Metal–organic framework derived nanomaterials for electrocatalysis: recent developments for CO₂ and N₂ reduction, *Nano Converg.*, 2021, **8**, 1–10.
- 13 D. Ongari, L. Talirz and B. Smit, Too Many Materials and Too Many Applications: An Experimental Problem Waiting for a Computational Solution, *ACS Cent. Sci.*, 2020, **6**, 1890–1900.
- 14 J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability, *J. Am. Chem. Soc.*, 2008, **130**, 47.
- 15 M. Kandiah, M. Hellner Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. Alessandra Quadrelli, F. Bonino and K. Petter Lillerud, Synthesis and

- Stability of Tagged UiO-66 Zr-MOFs, *Chem. Mater.*, 2010, **22**, 6632–6640.
- 16 Q. Chen, Q. He, M. Lv, Y. Xu, H. Yang, X. Liu and F. Wei, c, *Appl. Surf. Sci.*, 2015, **327**, 77–85.
 - 17 S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, A chemically functionalizable nanoporous material [Cu₃(TMA)₂(H₂O)₃](n), *Science*, 1999, **283**, 1148–1150.
 - 18 A. M. P. Peedikakkal and I. H. Aljundi, Mixed-Metal Cu-BTC Metal-Organic Frameworks as a Strong Adsorbent for Molecular Hydrogen at Low Temperatures, *ACS Omega*, 2020, **5**, 28493–28499.
 - 19 J. A. Hurd, R. Vaidhyanathan, V. Thangadurai, C. I. Ratcliffe, I. L. Moudrakovski and G. K. H. Shimizu, Anhydrous proton conduction at 150 °C in a crystalline metal–organic framework, *Nat. Chem.*, 2009, **1**, 705–710.
 - 20 D. W. Lim and H. Kitagawa, Proton Transport in Metal-Organic Frameworks, *Chem. Rev.*, 2020, **120**, 8416–8467.
 - 21 D. W. Lim and H. Kitagawa, Rational strategies for proton-conductive metal-organic frameworks Rational strategies for proton-conductive metal-organic frameworks, *Chem. Soc. Rev.*, 2021, **50**, 6349.
 - 22 K. Biradha, A. Goswami, R. Moi and S. Saha, Metal–organic frameworks as proton conductors: strategies for improved proton conductivity, *Dalt. Trans.*, 2021, **50**, 10655–10673.
 - 23 Y. Ye, L. Gong, S. Xiang, Z. Zhang, B. Chen, Y. Ye, L. Gong, S. Xiang, Z. Zhang and B. Chen, Metal-Organic Frameworks as a Versatile Platform for Proton Conductors, *Adv. Mater.*, 2020, **32**, 1907090.
 - 24 W. Zhang, R. Taheri-Ledari, M. Saeidirad, F. S. Qazi, A. Kashtiaray, F. Ganjali, Y. Tian and A. Maleki, Regulation of Porosity in MOFs: A Review on Tunable Scaffolds and Related Effects and Advances in Different Applications, *J. Environ. Chem. Eng.*, 2022, **10**, 108836.
 - 25 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter and O. M. Yaghi, Systematic design of pore size and functionality in isorecticular MOFs and their application in methane storage, *Science*, 2002, **295**, 469–472.
 - 26 Y. Yan, M. Juriček, F. X. Coudert, N. A. Vermeulen, S. Grunder, A. Dailly, W. Lewis, A. J. Blake, J. F. Stoddart and M. Schröder, Non-Interpenetrated Metal-Organic Frameworks Based on Copper(II) Paddlewheel and Oligoparaxylene-Isophthalate Linkers: Synthesis, Structure, and Gas Adsorption, *J. Am. Chem. Soc.*, 2016, **138**, 3371–3381.
 - 27 P. Li, Q. Chen, T. C. Wang, N. A. Vermeulen, B. L. Mehdi, A. Dohnalkova, N. D. Browning, D. Shen, R. Anderson, D. A. Gómez-Gualdrón, F. M. Cetin, J. Jagiello, A. M. Asiri, J. F. Stoddart and O. K. Farha, Hierarchically Engineered Mesoporous Metal-Organic Frameworks toward Cell-free Immobilized Enzyme Systems, *Chem*, 2018, **4**, 1022–1034.
 - 28 H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F.

- Gándara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O’Keeffe, O. Terasaki, J. F. Stoddart and O. M. Yaghi, Large-pore apertures in a series of metal-organic frameworks, *Science*, 2012, **336**, 1018–1023.
- 29 T.-F. Liu, D. Feng, Y.-P. Chen, L. Zou, M. Bosch, S. Yuan, Z. Wei, S. Fordham, K. Wang and H.-C. Zhou, Topology-Guided Design and Syntheses of Highly Stable Mesoporous Porphyrinic Zirconium Metal–Organic Frameworks with High Surface Area, *J. Am. Chem. Soc.*, 2014, **137**, 413–419.
 - 30 D. Perl, S. J. Lee, A. Ferguson, G. B. Jameson and S. G. Telfer, Hetero-interpenetrated metal-organic frameworks, *Nat. Chem.*, 2023, **15**, 1358–1364.
 - 31 Y.-N. Gong, D.-C. Zhong and T.-B. Lu, Interpenetrating metal-organic frameworks, *CrystEngComm*, 2016, **18**, 2596.
 - 32 G. Verma, S. Butikofer, S. Kumar and S. Ma, Regulation of the Degree of Interpenetration in Metal-Organic Frameworks, 2020, **378**, 4.
 - 33 D. J. Lun, G. I. N. Waterhouse and S. G. Telfer, A General Thermolabile Protecting Group Strategy for Organocatalytic Metal-Organic Frameworks, *J. Am. Chem. Soc.*, 2011, **133**, 5806–5809.
 - 34 J. J. Zhang, L. Wojtas, R. W. Larsen, M. Eddaoudi and M. J. Zaworotko, Temperature and concentration control over interpenetration in a metal-organic material, *J. Am. Chem. Soc.*, 2009, **131**, 17040–17041.
 - 35 S. K. Elsaidi, M. H. Mohamed, L. Wojtas, A. Chanthapally, T. Pham, B. Space, J. J. Vittal and M. J. Zaworotko, Putting the Squeeze on CH₄ and CO₂ through Control over Interpenetration in Diamondoid Nets, *J. Amer.*, 2014, **136**, 5072–5077.
 - 36 A. Schoedel, in *Metal-Organic Frameworks for Biomedical Applications*, Woodhead Publishing, 2020, pp. 11–44.
 - 37 M. Wang, R. Dong and X. Feng, Two-dimensional conjugated metal-organic frameworks (2D c-MOFs): chemistry and function for MOFtronics, *Chem. Soc. Rev.*, 2021, **50**, 2764.
 - 38 X. Wang, T. Qin, S.-S. Bao, Y.-C. Zhang, X. Shen, L.-M. Zheng and D. Zhu, Facile synthesis of a water stable 3D Eu-MOF showing high proton conductivity and its application as a sensitive luminescent sensor for Cu²⁺ ions, *J. Mater. Chem. A*, 2016, **4**, 16484.
 - 39 B. Chen, M. Eddaoudi, T. M. Reineke, J. W. Kampf, M. O’keeffe and O. M. Yaghi, Cu₂(ATC).6H₂O: Design of Open Metal Sites in Porous Metal-Organic Crystals (ATC: 1,3,5,7-Adamantane Tetracarboxylate), *J. Am. Chem. Soc.*, 2000, **122**, 11559–11560.
 - 40 H. Li, M. Eddaoudi, M. O’Keeffe and O. M. Yaghi, Design and synthesis of an exceptionally stable and highly porous metal-organic framework, *Nat.* 1999 4026759, 1999, **402**, 276–279.
 - 41 A. C. Sudik, A. P. Côté and O. M. Yaghi, Metal-organic frameworks based on trigonal prismatic building blocks and the new ‘acs’ topology, *Inorg. Chem.*, 2005, **44**, 2998–3000.

- 42 S. Biswas, M. Grzywa, H. P. Nayek, S. Dehnen, I. Senkovska, S. Kaskel and D. Volkmer, A cubic coordination framework constructed from benzobistriazolate ligands and zinc ions having selective gas sorption properties, *Dalt. Trans.*, 2009, **33**, 6487–6495.
- 43 R. Sen, D. Saha and S. Koner, Lanthanide carboxylate frameworks: Efficient heterogeneous catalytic system for epoxidation of olefins, *Catal. Letters*, 2012, **142**, 124–130.
- 44 D. Pugh, E. Ashworth, K. Robertson, L. C. Delmas, A. J. P. White, P. N. Horton, G. J. Tizzard, S. J. Coles, P. D. Lickiss and R. P. Davies, Metal–Organic Frameworks Constructed from Group 1 Metals (Li, Na) and Silicon-Centered Linkers, *Cryst. Growth Des.*, 2019, **19**, 6.
- 45 N. Király, D. Capková, R. Gyepes, N. Vargová, T. Kazda, J. Bednarčík, D. Yudina, T. Zelenka, P. Čudek, V. Zeleňák, A. Sharma, V. Meynen, V. Hornebecq, A. Straková Fedorková and M. Almáši, Sr(II) and Ba(II) Alkaline Earth Metal-Organic Frameworks (AE-MOFs) for Selective Gas Adsorption, Energy Storage, and Environmental Application, *Nanomaterials*, 2023, **13**, 234.
- 46 T. Steenhaut, Y. Filinchuk and S. Hermans, Aluminium-based MIL-100(Al) and MIL-101(Al) metal-organic frameworks, derivative materials and composites: synthesis, structure, properties and applications, *J. Mater. Chem. A*, 2021, **9**, 21483–21509.
- 47 B. Zhang, W. Wang, B. Liu and L. Hou, Indium metal-organic frameworks based on pyridylcarboxylate ligands and their potential applications, *Dalt. Trans.*, 2021, **50**, 5713.
- 48 H. Li, L. Li, R.-B. Lin, W. Zhou, Z. Zhang, S. Xiang and B. Chen, Porous metal-organic frameworks for gas storage and separation: Status and challenges, *Energy Chem*, 2019, **1**, 100006.
- 49 D. Zhao, X. Wang, L. Yue, Y. He and B. Chen, Porous metal-organic frameworks for hydrogen storage, *Chem. Commun*, 2022, **58**, 11059.
- 50 X. Zhang, P. Liu and Y. Zhang, The application of MOFs for hydrogen storage, *Inorganica Chim. Acta*, 2023, **557**, 121683.
- 51 D. Z. Li, L. Chen, G. Liu, Z. Y. Yuan, B. F. Li, X. Zhang and J. Q. Wei, Porous metal–organic frameworks for methane storage and capture: status and challenges, *New Carbon Mater.*, 2021, **36**, 468–496.
- 52 S. Mahajan and M. Lahtinen, Recent progress in metal-organic frameworks (MOFs) for CO₂ capture at different pressures, *J. Environ. Chem. Eng.*, 2022, **10**, 108930.
- 53 E. Martínez-Ahumada, M. L. Díaz-Ramírez, M. de J. Velásquez-Hernández, V. Jancik and I. A. Ibarra, Capture of toxic gases in MOFs: SO₂, H₂S, NH₃ and NO_x, *Chem. Sci.*, 2021, **12**, 6772–6799.
- 54 Y. H. Cheung, K. Ma, H. C. Van Leeuwen, M. C. Wasson, X. Wang, K. B. Idrees, W. Gong, R. Cao, J. J. Mahle, T. Islamoglu, G. W. Peterson, M. C. De Koning, J. H. Xin and O. K. Farha, Immobilized Regenerable Active Chlorine within a Zirconium-Based MOF Textile Composite to Eliminate Biological and Chemical Threats, *J. Am.*

- Chem. Soc.*, 2021, **143**, 16777–16785.
- 55 J. Bedia, V. Muelas-Ramos, M. Peñas-Garzón, A. Gómez-Avilés, J. J. Rodriguez and C. Belver, in *Nanomaterials for the Detection and Removal of Wastewater Pollutants*, Elsevier, 2020, pp. 241–283.
 - 56 F. Zadehahmadi, N. T. Eden, H. Mahdavi, K. Konstas, J. I. Mardel, M. Shaibani, P. C. Banerjee and M. R. Hill, Removal of metals from water using MOF-based composite adsorbents, *Environ. Sci. Water Res. Technol.*, 2023, **9**, 1305–1330.
 - 57 F. Hooriabad Saboor, N. Nasirpour, S. Shahsavari and H. Kazemian, The Effectiveness of MOFs for the Removal of Pharmaceuticals from Aquatic Environments: A Review Focused on Antibiotics Removal, *Chem. – An Asian J.*, 2022, **17**, 2021011.
 - 58 S. M. Sheta, M. A. Hamouda, O. I. Ali, A. T. Kandil, R. R. Sheha and S. M. El-Sheikh, Recent progress in high-performance environmental impacts of the removal of radionuclides from wastewater based on metal-organic frameworks: a review, *RSC Adv*, 2023, **13**, 25182–25208.
 - 59 F. Luo, X. Liang, W. Chen, S. Wang, X. Gao, Z. Zhang and Y. Fang, High-efficient and scalable solar-driven MOF-based water collection unit: From module design to concrete implementation, *Chem. Eng. J.*, 2023, **465**, 142891.
 - 60 W. Xu and O. M. Yaghi, Metal-Organic Frameworks for Water Harvesting from Air, Anywhere, Anytime, *ACS Cent. Sci.*, 2020, **6**, 1348–1354.
 - 61 W. Song, Z. Zheng, A. H. Alawadhi and O. M. Yaghi, MOF water harvester produces water from Death Valley desert air in ambient sunlight, *Nat. Water*, 2023, **1**, 626–634.
 - 62 C. Pontremoli, X. Qi, N. Shen, A. Al Othman, A. Mezentssev, A. Permyakova, Z. Yu, M. Lepoitevin, C. Serre and M. Durymanov, Metal-Organic Framework-Based Nanomedicines for the Treatment of Intracellular Bacterial Infections, *Pharmaceutics*, 2023, **15**, 1521.
 - 63 Y. Zhou, T. Yang, K. Liang and R. Chandrawati, Metal-organic frameworks for therapeutic gas delivery, *Adv. Drug Deliv. Rev.*, 2021, **171**, 199–214.
 - 64 H. D. Lawson, S. P. Walton and C. Chan, Metal-Organic Frameworks for Drug Delivery: A Design Perspective, *ACS Appl. Mater. Interfaces*, 2021, **13**, 7004–7020.
 - 65 D. Yang and B. C. Gates, Catalysis by Metal Organic Frameworks: Perspective and Suggestions for Future Research, *ACS Catal.*, 2019, **9**, 1779–1798.
 - 66 D. Narváez, N. Narváez-Celada and A. S. Varela, CO₂ electrochemical reduction on metal-organic framework catalysts: current status and future directions, *J. Mater. Chem. A*, 2022, **10**, 5899.
 - 67 H. H. Do, T. H. C. Nguyen, T. Van Nguyen, C. Xia, D. L. T. Nguyen, P. Raizada, P. Singh, V. H. Nguyen, S. H. Ahn, S. Y. Kim and Q. Van Le, Metal-organic-framework based catalyst for hydrogen production: Progress and perspectives, *Int. J. Hydrogen Energy*, 2022, **47**, 37552–37568.
 - 68 T. A. Goetjen, J. Liu, Y. Wu, J. Sui, X. Zhang, J. T. Hupp and O. K. Farha, Metal-organic framework (MOF) materials as polymerization catalysts: a review and recent

- advances, *Chem. Commun.*, 2020, **56**, 10409–10418.
- 69 G. An, X. Zhang, C. Zhang, H. Gao, S. Liu, G. Qin, H. Qi, J. Kasemchainan, J. Zhang and G. Wang, Metal-organic-framework-based materials as green catalysts for alcohol oxidation, *Chinese J. Catal.*, 2023, **50**, 126–174.
 - 70 A. Sarkar, S. Mistry, S. Bhattacharya and S. Natarajan, Multistep Cascade Catalytic Reactions Employing Bifunctional Framework Compounds, *Inorg. Chem.*, 2023, **62**, 11142–11151.
 - 71 S. Navalón, M. Álvaro, A. Dhakshinamoorthy and H. García, Encapsulation of Metal Nanoparticles within Metal–Organic Frameworks for the Reduction of Nitro Compounds, *Molecules*, 2019, **24**, 3050.
 - 72 Z. Fan, L. Staiger, K. Hemmer, Z. Wang, W. Wang, Q. Xie, L. Zhang, A. Urstoege, M. Schuster, J. A. Lercher, M. Cokoja and R. A. Fischer, Enhanced catalytic performance of palladium nanoparticles in MOFs by channel engineering, *Cell Reports Phys. Sci.*, 2022, **3**, 100757.
 - 73 T. Man, C. Xu, X. Y. Liu, D. Li, C. K. Tsung, H. Pei, Y. Wan and L. Li, Hierarchically encapsulating enzymes with multi-shelled metal-organic frameworks for tandem biocatalytic reactions, *Nat. Commun.*, 2022, **13**, 305.
 - 74 W. Wang, D. Chen, F. Li, X. Xiao and Q. Xu, Metal-organic-framework-based materials as platforms for energy applications, *Chem*, 2024, **10**, 86–133.
 - 75 S. Guo, Y. Xiao, J. Wang, Y. Ouyang, X. Li, H. Deng, W. He, Q. Zeng, W. Zhang, Q. Zhang and S. Huang, Ordered structure of interlayer constructed with metal-organic frameworks improves the performance of lithium-sulfur batteries, *Nano Res.*, 2021, **14**, 4556–4562.
 - 76 H. Bin Son, S. Cho, K. Baek, J. Jung, S. Nam, D. Y. Han, S. J. Kang, H. R. Moon and S. Park, All-Impurities Scavenging, Safe Separators with Functional Metal-Organic-Frameworks for High-Energy-Density Li-Ion Battery, *Adv. Funct. Mater.*, 2023, **33**, 2302563.
 - 77 M. Cheng, L. Kong, J. Zhu and X. H. Bu, in *Metal-Organic Framework-Based Nanomaterials for Energy Conversion and Storage*, Elsevier, 2022, pp. 341–362.
 - 78 R. Zhao, Y. Wu, Z. Liang, L. Gao, W. Xia, Y. Zhao and R. Zou, Metal-organic frameworks for solid-state electrolytes, *Environ. Sci.*, 2020, **13**, 2386–2403.
 - 79 M. Ko, L. Mendecki and K. A. Mirica, Conductive two-dimensional metal-organic frameworks as multifunctional materials, *Chem. Commun.*, 2018, **54**, 7873–7891.
 - 80 H. Yuan, N. Li, W. Fan, H. Cai and D. Zhao, Metal-Organic Framework Based Gas Sensors, *Adv. Sci.*, 2022, **9**, 2104374.
 - 81 S. K. Bhardwaj, N. Bhardwaj, R. Kaur, J. Mehta, A. L. Sharma, K. H. Kim and A. Deep, An overview of different strategies to introduce conductivity in metal-organic frameworks and miscellaneous applications thereof, *J. Mater. Chem. A*, 2018, **6**, 14992–15009.
 - 82 P. Qin, S. Okur, Y. Jiang and L. Heinke, A MOF-based electronic nose for carbon dioxide sensing with enhanced affinity and selectivity by ionic-liquid embedment, *J.*

- Mater. Chem. A*, 2022, **10**, 25347–25355.
- 83 G. Lu and J. T. Hupp, Metal-Organic Frameworks as Sensors: A ZIF-8 Based Fabry-Pérot Device as a Selective Sensor for Chemical Vapors and Gases, *J. Am. Chem. Soc.*, 2010, **132**, 7832–7833.
 - 84 F. M. Hinterholzinger, A. Ranft, J. M. Feckl, B. Ruhle, T. Bein and B. V Lotsch, One-dimensional metal-organic framework photonic crystals used as platforms for vapor sorption, *J. Mater. Chem.*, 2012, **22**, 10356.
 - 85 A. Ranft, F. Niekiet, I. Pavlichenko, N. Stock and B. V. Lotsch, Tandem MOF-based photonic crystals for enhanced analyte-specific optical detection, *Chem. Mater.*, 2015, **27**, 1961–1970.
 - 86 K. J. Kim, P. Lu, J. T. Culp and P. R. Ohodnicki, Metal-Organic Framework Thin Film Coated Optical Fiber Sensors: A Novel Waveguide-Based Chemical Sensing Platform, *ACS Sensors*, 2018, **3**, 386–394.
 - 87 S. I. Ohira, Y. Miki, T. Matsuzaki, N. Nakamura, Y. ki Sato, Y. Hirose and K. Toda, A fiber optic sensor with a metal organic framework as a sensing material for trace levels of water in industrial gases, *Anal. Chim. Acta*, 2015, **886**, 188–193.
 - 88 K. J. Kim, J. T. Culp, P. R. Ohodnicki, P. C. Cvetic, S. Sanguinito, A. L. Goodman and H. T. Kwon, Alkylamine-Integrated Metal-Organic Framework-Based Waveguide Sensors for Efficient Detection of Carbon Dioxide from Humid Gas Streams, *ACS Appl. Mater. Interfaces*, 2019, **11**, 33489–33496.
 - 89 J. Hromadka, B. Tokay, S. James, R. P. Tatam and S. Korposh, Optical fibre long period grating gas sensor modified with metal organic framework thin films, *Sensors Actuators B Chem.*, 2015, **221**, 891–899.
 - 90 B. Liedberg, C. Nylander and I. Lunström, Surface plasmon resonance for gas detection and biosensing, *Sensors and Actuators*, 1983, **4**, 299–304.
 - 91 Y. Shen, A. Tissot and C. Serre, Recent progress on MOF-based optical sensors for VOC sensing, *Chem. Sci.*, 2022, **13**, 13978–14007.
 - 92 W. Vandezande, K. P. F. Janssen, F. Delport, R. Ameloot, D. E. De Vos, J. Lammertyn and M. B. J. Roeffaers, Parts per Million Detection of Alcohol Vapors via Metal Organic Framework Functionalized Surface Plasmon Resonance Sensors, *Anal. Chem.*, 2017, **89**, 4480–4487.
 - 93 C. Y. Liu, X. R. Chen, H. X. Chen, Z. Niu, H. Hirao, P. Braunstein and J. P. Lang, Ultrafast Luminescent Light-Up Guest Detection Based on the Lock of the Host Molecular Vibration, *J. Am. Chem. Soc.*, 2020, **142**, 6690–6697.
 - 94 L. Sun, Y. Zhang, X. sen Lv and H. da Li, A luminescent Eu-based MOFs material for the sensitive detection of nitro explosives and development of fingerprint, *Inorg. Chem. Commun.*, 2023, **156**, 111267.
 - 95 T. Burger, M. V. Hernández, C. Carbonell, J. Rattenberger, H. Wilsche, P. Falcaro, C. Slugovc and S. M. Borisov, Luminescent Porphyrinic Metal-Organic Frameworks for Oxygen Sensing: Correlation of Nanostructure and Sensitivity, *ACS Appl. Nano Mater.*, 2023, **6**, 248–260.

- 96 Z. Long, L. Kou, M. J. Sepaniak and X. Hou, Recent advances in gas phase microcantileverbased sensing, *Rev. Anal. Chem.*, 2013, **32**, 135–158.
- 97 A. S. S. Vasan, D. M. Mahadeo, R. Doraiswami, Y. Huang and M. Pecht, Point-of-care biosensor system, *Front. Biosci. - Sch. Ed.*, 2013, **5**, 39–71.
- 98 M. D. Allendorf, R. J. T. Houk, L. Andruszkiewicz, A. A. Talin, J. Pikarsky, A. Choudhury, K. A. Gall and P. J. Hesketh, Stress-induced chemical detection using flexible metal-organic frameworks, *J. Am. Chem. Soc.*, 2008, **130**, 14404–14405.
- 99 C. Yim, M. Lee, M. Yun, G. H. Kim, K. T. Kim and S. Jeon, CO₂-Selective nanoporous metal-organic framework microcantilevers, *Sci. Rep.*, 2015, **5**, 10674.
- 100 T. Xu, P. Xu, D. Zheng, H. Yu and X. Li, Metal-organic frameworks for resonant-gravimetric detection of trace-level xylene molecules, *Anal. Chem.*, 2016, **88**, 12234–12240.
- 101 A. Pereira and L. F. Melo, in *Biofilms in the Food and Beverage Industries*, Elsevier Inc., 2009, pp. 131–151.
- 102 H. Uehara, St Ephane Diring, S. Furukawa, Z. Kalay, M. Tsotsalas, M. Nakahama, K. Hirai, M. Kondo, O. Sakata and S. Kitagawa, Porous Coordination Polymer Hybrid Device with Quartz Oscillator: Effect of Crystal Size on Sorption Kinetics, *J. Am. Chem. Soc.*, 2011, **133**, 30.
- 103 B. Liu, M. Tu and R. A. Fischer, Metal-organic framework thin films: Crystallite orientation dependent adsorption, *Angew. Chemie - Int. Ed.*, 2013, **52**, 3402–3405.
- 104 J. Devkota, P. R. Ohodnicki and D. W. Greve, SAW sensors for chemical vapors and gases, *Sensors*, 2017, **17**, 801.
- 105 A. Mujahid and F. L. Dickert, Surface acousticwave (SAW) for chemical sensing applications of recognition layers, *Sensors*, 2017, **17**, 2716.
- 106 F. L. Dickert, P. Forth, W. E. Bulst, G. Fischerauer and U. Knauer, SAW devices-sensitivity enhancement in going from 80 MHz to 1 GHz, *Sensors Actuators, B Chem.*, 1998, **46**, 120–125.
- 107 B. Paschke, A. Wixforth, D. Denysenko and D. Volkmer, Fast Surface Acoustic Wave-Based Sensors to Investigate the Kinetics of Gas Uptake in Ultra-Microporous Frameworks, *ACS Sensors*, 2017, **2**, 740–747.
- 108 S. Achmann, G. Hagen, J. Kita, I. M. Malkowsky, C. Kiener and R. Moos, Metal-Organic frameworks for sensing applications in the gas phase, *Sensors*, 2009, **9**, 1574–1589.
- 109 O. Yassine, O. Shekhah, A. H. Assen, Y. Belmabkhout, K. N. Salama and M. Eddaoudi, H₂S Sensors: Fumarate-Based fcu-MOF Thin Film Grown on a Capacitive Interdigitated Electrode, *Angew. Chemie Int. Ed.*, 2016, **55**, 15879–15883.
- 110 H. Yuan, G. Liu, Z. Qiao, N. Li, J. S. Buenconsejo, S. Xi, A. Karmakar, M. Li, H. Cai, S. J. Pennycook, D. Zhao, H. Yuan, G. Liu, A. Karmakar, D. Zhao, Z. Qiao, N. Li, H. Cai, P. J. S. Buenconsejo, S. Xi, M. Li and S. J. Pennycook, Solution-Processable Metal-Organic Framework Nanosheets with Variable Functionalities, *Adv. Mater.*, 2021, **33**, 2101257.

- 111 I. Stassen, B. Bueken, H. Reinsch, J. F. M. Oudenhoven, D. Wouters, J. Hajek, V. Van Speybroeck, N. Stock, P. M. Vereecken, R. Van Schaijk, D. De Vos and R. Ameloot, Towards metal-organic framework based field effect chemical sensors: UiO-66-NH₂ for nerve agent detection, *Chem. Sci.*, 2016, **7**, 5827–5832.
- 112 P. Davydovskaya, R. Pohle, A. Tawil and M. Fleischer, Work function based gas sensing with Cu-BTC metal-organic framework for selective aldehyde detection, *Sensors Actuators B*, 2013, **187**, 142–146.
- 113 S. Takaishi, M. Hosoda, T. Kajiwara, H. Miyasaka, M. Yamashita, Y. Nakanishi, Y. Kitagawa, K. Yamaguchi, A. Kobayashi and H. Kitagawa, Electroconductive porous coordination polymer Cu[Cu(pdt)₂] composed of donor and acceptor building units, *Inorg. Chem.*, 2009, **48**, 9048–9050.
- 114 L. S. Xie, G. Skorupskii and M. Dincă, Electrically Conductive Metal–Organic Frameworks, *Chem. Rev.*, 2020, **120**, 8536–8580.
- 115 C. Kittel, *Introduction to Solid State Physics*, John Wiley & Sons, Ltd, 2005.
- 116 L. Sun, C. H. Hendon, M. A. Minier, A. Walsh and M. Dincă, Million-fold electrical conductivity enhancement in Fe₂(DEBDC) versus Mn₂(DEBDC) (E = S, O), *J. Am. Chem. Soc.*, 2015, **137**, 6164–6167.
- 117 F. Gándara, F. J. Uribe-Romo, D. K. Britt, H. Furukawa, L. Lei, R. Cheng, X. Duan, M. O’Keeffe and O. M. Yaghi, Porous, conductive metal-triazolates and their structural elucidation by the charge-flipping method, *Chem. - A Eur. J.*, 2012, **18**, 10595–10601.
- 118 R. Dong, Z. Zhang, D. C. Tranca, S. Zhou, M. Wang, P. Adler, Z. Liao, F. Liu, Y. Sun, W. Shi, Z. Zhang, E. Zschech, S. C. B. Mannsfeld, C. Felser and X. Feng, A coronene-based semiconducting two-dimensional metal-organic framework with ferromagnetic behavior, *Nat. Commun.*, 2018, **9**, 2637.
- 119 J. Liu, X. Song, T. Zhang, S. Liu, H. Wen and L. Chen, 2D Conductive Metal–Organic Frameworks: An Emerging Platform for Electrochemical Energy Storage, *Angew. Chemie Int. Ed.*, 2021, **60**, 5612–5624.
- 120 M. Ko, L. Mendecki and K. A. Mirica, Conductive Two-Dimensional Metal-Organic Frameworks as Multifunctional Materials, *Chem. Commun*, 2018, **54**, 7873–7891.
- 121 S. Li, L. Xie, M. He, X. Hu, G. Luo, C. Chen and Z. Zhu, Metal-Organic frameworks-derived bamboo-like CuO/In₂O₃ Heterostructure for high-performance H₂S gas sensor with Low operating temperature, *Sensors Actuators, B Chem.*, 2020, **310**, 127828.
- 122 Z. Meng, R. M. Stolz and K. A. Mirica, Two-Dimensional Chemiresistive Covalent Organic Framework with High Intrinsic Conductivity, *J. Am. Chem. Soc.*, 2019, **141**, 11929–11937.
- 123 B. F. Abrahams, T. A. Hudson, L. J. McCormick and R. Robson, Coordination polymers of 2,5-dihydroxybenzoquinone and chloranilic acid with the (10,3)- A topology, *Cryst. Growth Des.*, 2011, **11**, 2717–2720.
- 124 B. F. Abrahams, J. Coleiro, K. Ha, B. F. Hoskins, S. D. Orchard and R. Robson,

- Dihydroxybenzoquinone and chloranilic acid derivatives of rare earth metals, *J. Chem. Soc. Dalt. Trans.*, 2002, **8**, 1586–1594.
- 125 L. E. Darago, M. L. Aubrey, C. J. Yu, M. I. Gonzalez and J. R. Long, Electronic Conductivity, Ferrimagnetic Ordering, and Reductive Insertion Mediated by Organic Mixed-Valence in a Ferric Semiquinoid Metal-Organic Framework, *J. Am. Chem. Soc.*, 2015, **137**, 15703–15711.
- 126 V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey and J. L. Brédas, Charge transport in organic semiconductors, *Chem. Rev.*, 2007, **107**, 926–952.
- 127 L. S. Xie, E. V. Alexandrov, G. Skorupskii, D. M. Proserpio and M. Dincă, Diverse π – π stacking motifs modulate electrical conductivity in tetrathiafulvalene-based metal–organic frameworks, *Chem. Sci.*, 2019, **10**, 8558–8565.
- 128 L. Qu, H. Iguchi, S. Takaishi, F. Habib, C. F. Leong, D. M. D’alessandro, T. Yoshida, H. Abe, E. Nishibori and M. Yamashita, Porous Molecular Conductor: Electrochemical Fabrication of Through-Space Conduction Pathways among Linear Coordination Polymers, *J. Am. Chem. Soc.*, 2019, **141**, 6802–6806.
- 129 E. A. Dolgoplova, V. A. Galitskiy, C. R. Martin, H. N. Gregory, B. J. Yarbrough, A. M. Rice, A. A. Berseneva, O. A. Ejegbavwo, K. S. Stephenson, P. Kittikhunnatham, S. G. Karakalos, M. D. Smith, A. B. Greytak, S. Garashchuk and N. B. Shustova, Connecting Wires: Photoinduced Electronic Structure Modulation in Metal-Organic Frameworks, *J. Am. Chem. Soc.*, 2019, **141**, 5350–5358.
- 130 S. Dawood, R. Yarbrough, K. Davis and H. Rathnayake, Self-assembly and optoelectronic properties of isorecticular MOF nanocrystals, *Synth. Met.*, 2019, **252**, 107–112.
- 131 S. R. Ahrenholtz, C. C. Epley and A. J. Morris, Solvothermal preparation of an electrocatalytic metalloporphyrin MOF thin film and its redox hopping charge-transfer mechanism, *J. Am. Chem. Soc.*, 2014, **136**, 2464–2472.
- 132 Z. Yin, Q. X. Wang and M. H. Zeng, Iodine release and recovery, influence of polyiodide anions on electrical conductivity and nonlinear optical activity in an interdigitated and interpenetrated bipillared-bilayer metal-organic framework, *J. Am. Chem. Soc.*, 2012, **134**, 4857–4863.
- 133 C. Schneider, D. Ukaj, R. Koerver, A. A. Talin, G. Kieslich, S. P. Pujari, H. Zuilhof, M. D. Urgan Janek, J. Allendorf and R. A. Fischer, High electrical conductivity and high porosity in a Guest@MOF material: evidence of TCNQ ordering within Cu₃BTC₂ micropores, *Chem. Sci.*, 2018, **9**, 7405.
- 134 J. Liu, T. Wächter, A. Irmeler, P. G. Weidler, H. Gliemann, F. Pauly, V. Mugnaini, M. Zharnikov and C. Wöll, Electric transport properties of surface-anchored metal-organic frameworks and the effect of ferrocene loading, *ACS Appl. Mater. Interfaces*, 2015, **7**, 9824–9830.
- 135 Q. X. Wang and C. Y. Zhang, Oriented synthesis of one-dimensional polypyrrole molecule chains in a metal-organic framework, *Macromol. Rapid Commun.*, 2011, **32**, 1610–1614.
- 136 Y. Q. Hu, M. Q. Li, Y. Wang, T. Zhang, P. Q. Liao, Z. Zheng, X. M. Chen and Y. Z.

- Zheng, Direct Observation of Confined I^{•••} · · · I^{2•••} · · · I^{•••} Interactions in a Metal–Organic Framework: Iodine Capture and Sensing, *Chem. – A Eur. J.*, 2017, **23**, 8409–8413.
- 137 L. S. Xie, G. Skorupskii and M. Dincă, Electrically Conductive Metal–Organic Frameworks, *Chem. Rev.*, 2020, **120**, 8536–8580.
 - 138 L. Sun, M. G. Campbell and M. Dincă, Electrically Conductive Porous Metal–Organic Frameworks, *Angew. Chemie Int. Ed.*, 2016, **55**, 3566–3579.
 - 139 D. Sheberla, L. Sun, M. A. Blood-Forsythe, S. Leyman Er, C. R. Wade, C. K. Brozek, A. Alán Aspuru-Guzik and M. Dincă, High Electrical Conductivity in Ni₃(2,3,6,7,10,11-hexaiminotriphenylene)₂, a Semiconducting Metal–Organic Graphene Analogue, *J. Am. Chem. Soc.*, 2014, **3**, 8859–8862.
 - 140 J. Cui and Z. Xu, An electroactive porous network from covalent metal–dithiolene links, *Chem. Commun.*, 2014, **50**, 3986–3988.
 - 141 M. Hmadeh, Z. Lu, Z. Liu, F. G. Gándara, H. Furukawa, S. Wan, V. Augustyn, R. Chang, L. Liao, F. Zhou, E. Perre, V. Ozolins, K. Suenaga, X. Duan, B. Dunn, Y. Yamamoto, O. Terasaki and O. M. Yaghi, New Porous Crystals of Extended Metal–Catecholates, *Chem. Mater*, 2012, **24**, 3511–3513.
 - 142 R. W. Day, D. K. Bediako, M. Rezaee, L. R. Parent, G. Skorupskii, M. Q. Arguilla, C. H. Hendon, I. Stassen, N. C. Gianneschi, P. Kim and M. Dincă, Single Crystals of Electrically Conductive Two-Dimensional Metal–Organic Frameworks: Structural and Electrical Transport Properties, *ACS Cent. Sci.*, 2019, **5**, 1959–1964.
 - 143 R. M. Stolz, A. Mahdavi-Shakib, B. G. Frederick and K. A. Mirica, Host–Guest Interactions and Redox Activity in Layered Conductive Metal–Organic Frameworks, 2020, **32**, 7639–7652.
 - 144 V. Rubio-Giménez, N. Almora-Barrios, G. Escorcía-Ariza, M. Galbiati, M. Sessolo, S. Tatay and C. Martí-Gastaldo, Origin of the Chemiresistive Response of Ultrathin Films of Conductive Metal–Organic Frameworks, *Angew. Chemie - Int. Ed.*, 2018, **57**, 15086–15090.
 - 145 S. Chen, J. Dai and X. C. Zeng, Metal–organic Kagome lattices M₃(2,3,6,7,10,11-hexaiminotriphenylene)₂ (M = Ni and Cu): from semiconducting to metallic by metal substitution, *Phys. Chem. Chem. Phys.*, 2015, **17**, 5954–5958.
 - 146 V. Rubio-Giménez, M. Galbiati, J. Castells-Gil, N. Almora-Barrios, J. Navarro-Sánchez, G. Escorcía-Ariza, M. Mattera, T. Arnold, J. Rawle, S. Tatay, E. Coronado, C. Martí-Gastaldo, T. Arnold and J. Rawle, Bottom-Up Fabrication of Semiconductive Metal–Organic Framework Ultrathin Films, *Adv. Mater*, 2018, **30**, 1704291.
 - 147 M. E. Foster, K. Sohlberg, M. D. Allendorf and A. A. Talin, Unraveling the Semiconducting/Metallic Discrepancy in Ni₃(HITP)₂, *J. Phys. Chem. Lett.*, 2018, **9**, 481–486.
 - 148 M.-S. Yao, X.-J. Lv, Z.-H. Fu, W.-H. Li, W.-H. Deng, G.-D. Wu and G. Xu, Layer-by-Layer Assembled Conductive Metal–Organic Framework Nanofilms for Room-Temperature Chemiresistive Sensing, *Angew. Chemie*, 2017, **129**, 16737–16741.

- 149 M. De Lourdes Gonzalez-Juarez, C. Morales, J. I. Flege, E. Flores, M. Martin-Gonzalez, I. Nandhakumar and D. Bradshaw, Tunable Carrier Type of a Semiconducting 2D Metal–Organic Framework Cu₃(HHTP)₂, *ACS Appl. Mater. Interfaces*, 2022, **14**, 12404–12411.
- 150 L. Sun, B. Liao, D. Sheberla, D. Kraemer, J. Zhou, E. A. Stach, D. Zakharov, V. Stavila, A. A. Talin, Y. Ge, M. D. Allendorf, G. Chen, F. Léonard and M. Dincă, A Microporous and Naturally Nanostructured Thermoelectric Metal–Organic Framework with Ultralow Thermal Conductivity, *Joule*, 2017, **1**, 168–177.
- 151 G. Wu, J. Huang, Y. Zang, J. He and G. Xu, Porous field-effect transistors based on a semiconductive metal-organic framework, *J. Am. Chem. Soc.*, 2017, **139**, 1360–1363.
- 152 M. G. Campbell, S. F. Liu, T. M. Swager and M. Dincă, Chemiresistive Sensor Arrays from Conductive 2D Metal–Organic Frameworks, *J. Am. Chem. Soc.*, 2015, **137**, 13780–13783.
- 153 M. Ko, A. Aykanat, M. K. Smith and K. A. Mirica, Drawing Sensors with Ball-Milled Blends of Metal–Organic Frameworks and Graphite, *Sensors*, 2017, **17**, 2192.
- 154 A. Mahringer, A. C. Jakowetz, J. M. Rotter, B. J. Bohn, J. K. Stolarczyk, J. Feldmann, T. Bein and D. D. Medina, Oriented Thin Films of Electroactive Triphenylene Catecholate-Based Two-Dimensional MetalOrganic Frameworks, *ACS Nano*, 2019, **13**, 6711–6719.
- 155 J. Wu, J. Chen, C. Wang, Y. Zhou, K. Ba, H. Xu, W. Bao, X. Xu, A. Carlsson, S. Lazar, A. Meingast, Z. Sun and H. Deng, Metal–Organic Framework for Transparent Electronics, *Adv. Sci.*, 2020, **7**, 1903003.
- 156 M. Miao, Z. Wang, Z. Guo and J. Xing, Quasi Solid–Liquid Reaction Strategy to In Situ Synthesize the Conductive MOF Film with Ordered Submicron Macropores for Gas Sensing, *Adv. Mater. Interfaces*, 2022, **9**, 2101908.
- 157 J. O. Kim, W. T. Koo, H. Kim, C. Park, T. Lee, C. A. Hutomo, S. Q. Choi, D. S. Kim, I. D. Kim and S. Park, Large-area synthesis of nanoscopic catalyst-decorated conductive MOF film using microfluidic-based solution shearing, *Nat. Commun.*, 2021, **12**, 4294.
- 158 C. Sun, W. Wang, X. Mu, Y. Zhang, Y. Wang, C. Ma, Z. Jia, J. Zhu and C. Wang, Tuning the Electrical Conductivity of a Flexible Fabric-Based Cu-HHTP Film through a Novel Redox Interaction between the Guest-Host System, *ACS Appl. Mater. Interfaces*, 2022, **14**, 54266–54275.
- 159 A. M. Eagleton, M. Ko, R. M. Stolz, N. Vereshchuk, Z. Meng, L. Mendecki, A. M. Levenson, C. Huang, K. C. MacVeagh, A. Mahdavi-Shakib, J. J. Mahle, G. W. Peterson, B. G. Frederick and K. A. Mirica, Fabrication of Multifunctional Electronic Textiles Using Oxidative Restructuring of Copper into a Cu-Based Metal–Organic Framework, *J. Am. Chem. Soc.*, 2022, **144**, 23297–23312.
- 160 M. De Lourdes Gonzalez-Juarez, E. Flores, M. Martin-Gonzalez, I. Nandhakumar and D. Bradshaw, Electrochemical deposition and thermoelectric characterisation of a semiconducting 2-D metal-organic framework thin film, *J. Mater. Chem. A*, 2020, **8**, 13197–13206.

- 161 Y. Liu, Y. Wei, M. Liu, Y. Bai, X. Wang, S. Shang, J. Chen and Y. Liu, Electrochemical Synthesis of Large Area Two-Dimensional Metal–Organic Framework Films on Copper Anodes, *Angew. Chemie - Int. Ed.*, 2021, **60**, 2887–2891.
- 162 P. Li, X. Shi, Y. Wu, M. Song, Y. Lai, H. Yu and G. Lu, Cathodic synthesis of a Cu-catecholate metal–organic framework, *CrystEngComm*, 2021, **23**, 1828–1835.
- 163 M. G. Campbell, D. Sheberla, S. F. Liu, T. M. Swager and M. Dincă, Cu₃(hexaiminotriphenylene)₂ : An Electrically Conductive 2D Metal–Organic Framework for Chemiresistive Sensing, *Angew. Chemie Int. Ed.*, 2015, **54**, 4349–4352.
- 164 M. K. Smith, K. E. Jensen, P. A. Pivak and K. A. Mirica, Direct Self-Assembly of Conductive Nanorods of Metal–Organic Frameworks into Chemiresistive Devices on Shrinkable Polymer Films, *Chem. Mater.*, 2016, **28**, 5264–5268.
- 165 M. K. Smith and K. A. Mirica, Self-Organized Frameworks on Textiles (SOFT): Conductive Fabrics for Simultaneous Sensing, Capture, and Filtration of Gases, *J. Am. Chem. Soc.*, 2017, **139**, 16759–16767.
- 166 W.-T. Koo, S.-J. Kim, J.-S. Jang, D.-H. Kim, I.-D. Kim, W.-T. Koo, S.-J. Kim, J.-S. Jang, D.-H. Kim and I.-D. Kim, Catalytic Metal Nanoparticles Embedded in Conductive Metal–Organic Frameworks for Chemiresistors: Highly Active and Conductive Porous Materials, *Adv. Sci.*, 2019, **6**, 1900250.
- 167 Y.-M. Jo, K. Lim, J. Won Yoon, Y. Kun Jo, Y. Kook Moon, H. Won Jang and J.-H. Lee, Visible-Light-Activated Type II Heterojunction in Cu₃(hexahydroxytriphenylene)₂/Fe₂O₃ Hybrids for Reversible NO₂ Sensing: Critical Role of π – π^* Transition, *ACS Cent. Sci.*, 2021, **7**, 1176–1182.
- 168 B. Hoppe, K. D. J. Hindricks, D. P. Warwas, H. A. Schulze, A. Mohmeyer, T. J. Pinkvos, S. Zailskas, M. R. Krey, C. Belke, S. König, M. Fröba, R. J. Haug and P. Behrens, Graphene-like metal-organic frameworks: Morphology control, optimization of thin film electrical conductivity and fast sensing applications, *CrystEngComm*, 2018, **20**, 6458–6471.
- 169 P. J. Kelly and R. D. Arnell, Magnetron sputtering: a review of recent developments and applications, *Vacuum*, 2000, **56**, 159–172.
- 170 M. Ganeva, *Thesis: Formation of metal nano-size clusters with a DC magnetron-based gas aggregation source*, Ernst-Moritz-Arndt-Universität Greifswald, 2013.
- 171 A. Majumdar, D. Köpp, M. Ganeva, D. Datta, S. Bhattacharyya and R. Hippler, Development of metal nanocluster ion source based on dc magnetron plasma sputtering at room temperature, *Rev. Sci. Instrum.*, 2009, **80**, 095103.
- 172 Nikalyte, *NL50 Technical Note: Nanoparticle size control with the NL50*, 2021.
- 173 M. Ganeva, T. Peter, S. Bornholdt, H. Kersten, T. Strunskus, V. Zaporozhchenko, F. Faupel and R. Hippler, Mass Spectrometric Investigations of Nano-Size Cluster Ions Produced by High Pressure Magnetron Sputtering, *Contrib. to Plasma Phys.*, 2012, **52**, 881–889.
- 174 M. Mhadhbi, *Electron Microscopy*, IntechOpen, 2022.

- 175 M. Ohring, *Materials Science of Thin Films*, Elsevier Science, 2001.
- 176 A. Chauhan and P. Chauhan, Powder XRD Technique and its Applications in Science and Technology, *J. Anal. Bioanal. Tech.*, 2014, **5**, 212.
- 177 W. Clegg, *X-ray Crystallography*, Oxford Chemistry Primers, 2015.
- 178 S. P. Burrows, *Thesis: Infrared Spectroscopic Measurement of Titanium Dioxide Nanoparticle Shallow Trap State Energies*, Virginia Tech, 2010.
- 179 W. Zhou, Y. H. Ikuhara, Z. Zheng, K. Wang, B. Cao and J. Chen, *Transmission electron microscopy (TEM) studies of functional nanomaterials*, Woodhead Publishing, 2023.
- 180 N. John and S. George, *Raman Spectroscopy*, Elsevier, 2017, vol. 2.
- 181 M. H. Engelhard, T. C. Droubay and Y. Du, *X-Ray Photoelectron Spectroscopy Applications*, Academic Press, 2017.
- 182 B. Armitage, *Thesis: Vapour Detection of Explosives , Chemical Agents and Drugs*, University of Oxford, 2021.
- 183 G. L. Long and J. D. Winefordner, Limit of Detection: A Closer Look at the IUPAC Definition, *Anal. Chem.*, 1983, **55**, 713A-724A.
- 184 M. Rodner and J. Eriksson, First-order time-derivative readout of epitaxial graphene-based gas sensors for fast analyte determination, *Sensors and Actuators Reports*, 2020, **2**, 100012.
- 185 M. Kwoka and J. Szuber, Studies of NO₂ Gas-Sensing Characteristics of a Novel Room-Temperature Surface-Photovoltage Gas Sensor Device, *Sensors*, 2020, **20**, 408.
- 186 Y. Qu, W. Zhou, X. Miao, Y. Li, L. Jiang, K. Pan, G. Tian, Z. Ren, G. Wang and H. Fu, A New Layered Photocathode with Porous NiO Nanosheets: An Effective Candidate for p-Type Dye-Sensitized Solar Cells, *Chem. – An Asian J.*, 2013, **8**, 3085–3090.
- 187 J. L. Zhuang, D. Ar, X. J. Yu, J. X. Liu and A. Terfort, Patterned deposition of metal-organic frameworks onto plastic, paper, and textile substrates by inkjet printing of a precursor solution, *Adv. Mater.*, 2013, **25**, 4631–4635.
- 188 D. Cai, M. Lu, L. Li, J. Cao, D. Chen, H. Tu, J. Li and W. Han, A Highly Conductive MOF of Graphene Analogue Ni₃(HITP)₂ as a Sulfur Host for High-Performance Lithium–Sulfur Batteries, *Small*, 2019, **15**, 1902605.
- 189 J. Mu, X. Zhong, W. Dai, X. Pei, J. Sun, J. Zhang, W. Luo and W. Zhou, Metal-Organic Framework Assembled on Oriented Nanofiber Arrays for Field-Effect Transistor and Gas Sensor-Based Applications, *Molecules*, 2022, **27**, 2131.
- 190 M. Miao, Z. Wang, Z. Guo and J. Xing, Quasi Solid–Liquid Reaction Strategy to In Situ Synthesize the Conductive MOF Film with Ordered Submicron Macropores for Gas Sensing, *Adv. Mater. Interfaces*, 2022, **9**, 2101908.
- 191 A. P. Grosvenor, M. C. Biesinger, R. S. C. Smart and N. S. McIntyre, New interpretations of XPS spectra of nickel metal and oxides, *Surf. Sci.*, 2006, **600**, 1771–1779.

- 192 T. Chen, J. H. Dou, L. Yang, C. Sun, N. J. Libretto, G. Skorupskii, J. T. Miller and M. Dincă, Continuous Electrical Conductivity Variation in M₃(Hexaiminotriphenylene)₂ (M = Co, Ni, Cu) MOF Alloys, *J. Am. Chem. Soc.*, 2020, **142**, 12367–12373.
- 193 X. Chen, Y. Lu, J. Dong, L. Ma, Z. Yi, Y. Wang, L. Wang, S. Wang, Y. Zhao, J. Huang and Y. Liu, Ultrafast in Situ Synthesis of Large-Area Conductive Metal–Organic Frameworks on Substrates for Flexible Chemiresistive Sensing, *ACS Appl. Mater. Interfaces*, 2020, **12**, 57235–57244.
- 194 S. S. Yp. G. of M.-O. F. C. by E. S. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, Patterned Growth of Metal–Organic Framework Coatings by Electrochemical Synthesis, *J. Phys. Chem. C*, 2009, **21**, 2580–2582.
- 195 Z. Meng, R. M. Stolz and K. A. Mirica, Two-Dimensional Chemiresistive Covalent Organic Framework with High Intrinsic Conductivity, *J. Am. Chem. Soc.*, 2019, **141**, 58.
- 196 M.-S. Yao, X.-J. Lv, Z.-H. Fu, W.-H. Li, W.-H. Deng, G.-D. Wu, G. Xu, X. J. Lv, W. H. Li, W. H. Deng and G. D. W. G. Xu, Layer-by-Layer Assembled Conductive Metal–Organic Framework Nanofilms for Room-Temperature Chemiresistive Sensing, *Angew. Chemie - Int. Ed.*, 2017, **56**, 6510–16514.
- 197 M. A. Borysiewicz, J. H. Dou, I. Stassen and M. Dincă, Why conductivity is not always king – physical properties governing the capacitance of 2D metal–organic framework-based EDLC supercapacitor electrodes: a Ni₃(HITP)₂ case study, *Faraday Discuss.*, 2021, **231**, 298–304.
- 198 J. W. Gittins, C. J. Balhatchet, S. M. Fairclough and A. C. Forse, Enhancing the energy storage performances of metal–organic frameworks by controlling microstructure, *Chem. Sci.*, 2022, **13**, 9210–9219.
- 199 D. Bradshaw, S. El-Hankari and L. Lupica-Spagnolo, Supramolecular templating of hierarchically porous metal-organic frameworks, *Chem. Soc. Rev.*, 2014, **43**, 5431–5443.
- 200 J. Reboul, S. Furukawa, N. Horike, M. Tsotsalas, K. Hirai, H. Uehara, M. Kondo, N. Louvain, O. Sakata and S. Kitagawa, Mesoscopic architectures of porous coordination polymers fabricated by pseudomorphic replication, *Nat. Mater.*, 2012, **11**, 717–723.
- 201 R. M. Stolz, A. F. Kolln, B. C. Rocha, A. Brinks, A. M. Eagleton, L. Mendecki, H. Vashisth and K. A. Mirica, Epitaxial Self-Assembly of Interfaces of 2D Metal–Organic Frameworks for Electroanalytical Detection of Neurotransmitters, *ACS Nano*, 2022, **16**, 13869–13883.
- 202 Q. Qi, P. P. Wang, J. Zhao, L. L. Feng, L. J. Zhou, R. F. Xuan, Y. P. Liu and G. D. Li, SnO₂ nanoparticle-coated In₂O₃ nanofibers with improved NH₃ sensing properties, *Sensors Actuators, B Chem.*, 2014, **194**, 440–446.
- 203 R. Lewicki, A. A. Kosterev, D. M. Thomazy, T. H. Risby, S. Solga, T. B. Schwartz and F. K. Tittel, Real time ammonia detection in exhaled human breath using a distributed feedback quantum cascade laser based sensor, *Quantum Sens. Nanophotonic Devices VIII*, 2011, **7945**, 79450K.

- 204 M. J. Lefferts, L. H. Humphreys, N. Mai, K. Murugappan, B. I. Armitage, J.-F. Pons and M. R. Castell, ANFO vapour detection with conducting polymer percolation network sensors and GC/MS, 2021, **146**, 2186–2193.
- 205 M. Faeik, R. Al-Okby, S. Neubert, T. Roddelkopf and K. Thurow, in *IEEE 21st International Symposium on Computational Intelligence and Informatics*, 2021.
- 206 W. Li, M. J. Lefferts, B. I. Armitage, K. Murugappan and M. R. Castell, Polypyrrole Percolation Network Gas Sensors: Improved Reproducibility through Conductance Monitoring during Polymer Growth, *ACS Appl. Polym. Mater.*, 2022, **4**, 2216–2959.