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# **Green Synthesis of Zeolitic Imidazolate Frameworks (ZIFs) for Sustainable Development**

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The research described in this thesis is my original work. To the best of my knowledge and belief, it contains no materials previously published or written by another person, except where otherwise acknowledged.

Mahdiar Taheri  
January 2021

To  
*my wife, Elmira,*  
&  
*my parents!*

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## Abstract

Metal organic frameworks (MOFs) are a broad family of micro-/mesoporous materials with significant potential for energy storage, CO<sub>2</sub> capture, and environmental remediation due to their tunable pore size and very high surface area. In recent years, many nanofabrication methodologies to engineer MOFs have been investigated. Despite progress, it remains challenging to produce well-dispersed MOF nanopowders from an inexpensive precursor and to form three-dimensional MOF films with controlled porosity, hindering the use of MOFs in many applications. Furthermore, there are only a small number of studies that explored scalable and environmentally friendly synthesis routes. In order to utilise MOFs for sustainable development, it is of great importance to not only minimise the waste generation and environmental impacts in their syntheses, but also develop suitable applications to mitigate environmental damages, energy problems, and health risks.

This thesis focuses on zeolitic imidazolate frameworks (ZIFs), a subclass of the MOF family of materials, in particular ZIF-8 (made of Zn<sup>2+</sup> and 2-methylimidazolate) and cobalt-doped-ZIF-8. In this thesis, new approaches to synthesising ZIF-8 in powder and film forms were investigated using environmentally friendly methods, and their new applications in the energy and environmental sectors were explored.

In the first study, a green and scalable synthesis method was investigated to produce well-dispersed ZIF-8 nanopowders with a high yield and minimal waste, for applications in contaminant removal. It was demonstrated that mechanochemical processing of a stoichiometric ratio of ZnO nanoparticles and 2-methylimidazole results in the full conversion of ZnO nanopowders into ZIF-8 of ca 80 nm in diameter with little agglomeration. Dry reactive grinding and liquid assisted grinding were systematically investigated to identify optimum processing parameters. The application of mechanochemically synthesised ZIF-8 in water treatment was explored. It was found for the first time that mechanochemically-produced nanopowders have higher efficacy in adsorbing organic pollutants than ZIF-8

nanopowders synthesised via common solution-based methods, due to their unique surface characteristics.

In the second study, the conversion of highly porous films of ZnO nanoparticles into ZIF-8 films was studied. A new methodology was developed to structure MOFs into monolithic films with tunable extrinsic porosity. It was demonstrated for the first time that ZIF-8 films with uniform intergrown grains and structural porosity can be obtained from highly porous films of ZnO nanoparticles, via vapour-phase conversion of the metal oxide precursors. The hierarchically porous structure of ZIF-8 films was engineered into a wide range of porosity, from a dense film to a highly porous film, by controlling the reaction temperature. The use of the ZIF-8 monoliths in an energy application was studied: dense and crack-free ZIF-8 monoliths were used as molecular sieve separators in a model lithium-sulphur battery system, which significantly enhanced the long-term stability and performance of the battery system compared to other benchmark separators.

In the third study, the stability of ZIFs in water was studied using a new combination of analytical tools. It is widely believed that ZIFs have excellent structural stability in water and thus they are ideal for aqueous applications. However, recent studies found some evidence that ZIF-8 undergoes hydrolysis in water. Despite the importance of ZIF's stability in many aqueous applications, the extent of ZIFs' degradation in water is still not fully understood. This study demonstrated the importance of analysing both filtered powders and the filtrate liquid in water-stability tests, in particular using UV-Vis spectroscopy and thermogravimetric analysis. The new combination of analytical tools confirmed that ZIF-8 is unstable in water, and enabled the quantitative study of the effects of ZIF concentrations in water, cobalt doping levels, and amounts of ligands in water, on the water stability of ZIF samples. The effect of cobalt-doping levels was investigated using ZIF particles with identical sizes (200-400 nm), thereby eliminating the effects of particle size on hydrolysis. Unlike other synthesis methods, mechanochemical ball milling of the metal salt and the ligand allowed the production of nano-

scale ZIF-8 particles with similar sizes, independent of cobalt-doping levels. The proposed combination of analytical tools can be applied to the water stability study of other MOF materials.

In the last study, the instability of ZIF-8 in aqueous systems was utilised in a biomedical application. Taking advantage of the release of ZIFs' building blocks (i.e. zinc and 2-methylimidazole ions) in aqueous media, the antibacterial properties of ZIF-8 are studied against gram-negative *Escherichia coli* (*E. coli*) and their efficacy was compared with ZnO, a widely-used antimicrobial agent. It was demonstrated that the antibacterial properties of ZIF-8 are superior to ZnO. The reason was elucidated by investigating the stability of ZIF-8 in common culture media used in antibacterial tests, phosphate buffer saline (PBS) solution and Luria-Bertani (LB) broth. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) and UV-Vis absorption spectroscopy revealed that the degradation of ZIF-8 in the culture media is enhanced due to the reaction between  $\text{Zn}^{2+}$  released from ZIF-8 and phosphate ions in PBS, or organic moieties in LB broth, resulting in stronger antibacterial properties of ZIF-8 than that of ZnO. The results strongly advocate the importance of stability studies on MOFs in developing their biomedical applications, in terms of their efficacy, bio-safety, and eco-safety.

As an extension of this study, the use of ZIF-8 to supplement the antibacterial properties of superhydrophobic surfaces (SHSs) was studied. Sub-micron size ZIF-8 particles were incorporated in SHSs and the changes in the superhydrophobicity and antibacterial properties of the surfaces were analysed. The original SHS with a contact angle of  $157^\circ$  and a rolling angle of  $0^\circ$  prevents the adhesion of bacteria, however, after long submersion in water or scratching the surface, bacteria can colonise on the surface. The addition of ZIF-8 particles (up to 15 wt%) to the SHS imparted dual functionality to the surface, by introducing bactericidal properties while retaining the superhydrophobic properties (a contact angle greater than  $150^\circ$  and a rolling angle less than  $10^\circ$ ) to prevent bacterial adhesion.

The present thesis has made significant contributions to the progress of MOF research in the following manner: It developed new green techniques to synthesise free-standing MOF nanoparticles and hierarchical MOF films, which can be applied to the large-scale production of other MOFs. It obtained a new understanding of the advantages and limitations in the green syntheses of ZIF-8 from ZnO, one of the simplest and most inexpensive metal precursors. It demonstrated the tunability of their physical properties for sustainability-related applications such as energy storage and health security. It revealed the instability of ZIF-8 in different aqueous media, using a new set of quantitative techniques, which provides valuable guidelines to future investigations of MOFs' stability in aqueous media from the viewpoint of biosafety, eco-safety, and application development.

## Publications and Conferences

### Journal Publications

- **M. Taheri**, I Bernardo Di, A. Lowe, D. Nisbet, T. Tsuzuki “Green full conversion of ZnO nanopowders to well-dispersed zeolitic imidazolate framework-8 (ZIF-8) nanopowders via a stoichiometric mechanochemical reaction for fast dye adsorption”, *Crystal Growth & Design*, Vol. 20 (4), 2020, pp 2761-2773.
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## Conferences

- 8<sup>th</sup> International Conference on Nanoscience and Nanotechnology (ICONN 2020), February 2020, Brisbane, Australia; Oral Presentation
- 6<sup>th</sup> Nano Today Conference (NanoToday 2019), June 2019, Lisbon, Portugal; Poster Presentation (Finalist in the best poster award)
- 6<sup>th</sup> International Conference on Metal-Organic Frameworks (MOF 2018), December 2018, Auckland, New Zealand; Attendance
- 7<sup>th</sup> International Conference on Nanoscience and Nanotechnology (ICONN 2018), February 2018, Wollongong, Australia; Poster Presentation

## Journal Publications Unrelated to the Thesis

- Z. Fusco, **M. Taheri**, R. Bo, T. Tran-Phu, H. Chen, X. Guo, Y. Zhu, T. Tsuzuki, T. P. White, A. Tricoli “Non-Periodic Epsilon-Near-Zero Metamaterials at Visible Wavelengths for Efficient Non-Resonant Optical Sensing”, Nano Letters, Vol. 20 (5), 2020, pp 3970–3977.
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## List of Abbreviations

|                 |                                                            |
|-----------------|------------------------------------------------------------|
| BET             | Brunauer, Emmet and Teller surface area determination      |
| BPR             | Ball-to-powder ratio                                       |
| CO <sub>2</sub> | Carbon dioxide                                             |
| COD             | Crystallographic Open Database                             |
| CV              | Cyclic voltammetry                                         |
| DI              | Deionised water                                            |
| EDX             | Energy-dispersive X-ray spectroscopy                       |
| FTIR            | Fourier transform infrared                                 |
| HKUST           | Hong Kong University of Science and Technology             |
| ICP             | Inductively coupled plasma                                 |
| ICP-OES         | Inductively coupled plasma – optical emission spectroscopy |
| IR              | Infrared                                                   |
| MIL             | Matériaux de l'Institut Lavoisier                          |
| MOF             | Metal-Organic Framework                                    |
| PTFE            | Polytetrafluoroethylene                                    |
| PVDF            | Polyvinylidene fluoride                                    |
| PXRD            | Powder X-ray Diffraction                                   |
| SBU             | Secondary Building Units                                   |
| SEM             | Scanning electron microscopy                               |
| STEM            | Scanning transmission electron microscopy                  |
| SSA             | Specific surface area                                      |
| TEM             | Transmission Electron Microscopy                           |
| TGA             | Thermogravimetric Analysis                                 |
| UiO             | University of Oslo                                         |
| UV-Vis          | Ultraviolet-Visible                                        |
| UNN             | Ultraporous Nanoparticle Network                           |
| XPS             | X-ray photoelectron spectroscopy                           |
| XRD             | X-ray diffraction                                          |
| ZIF             | Zeolitic Imidazolate Framework                             |

# Chapter One

## Part (I) Introduction

### 1.1 Motivation

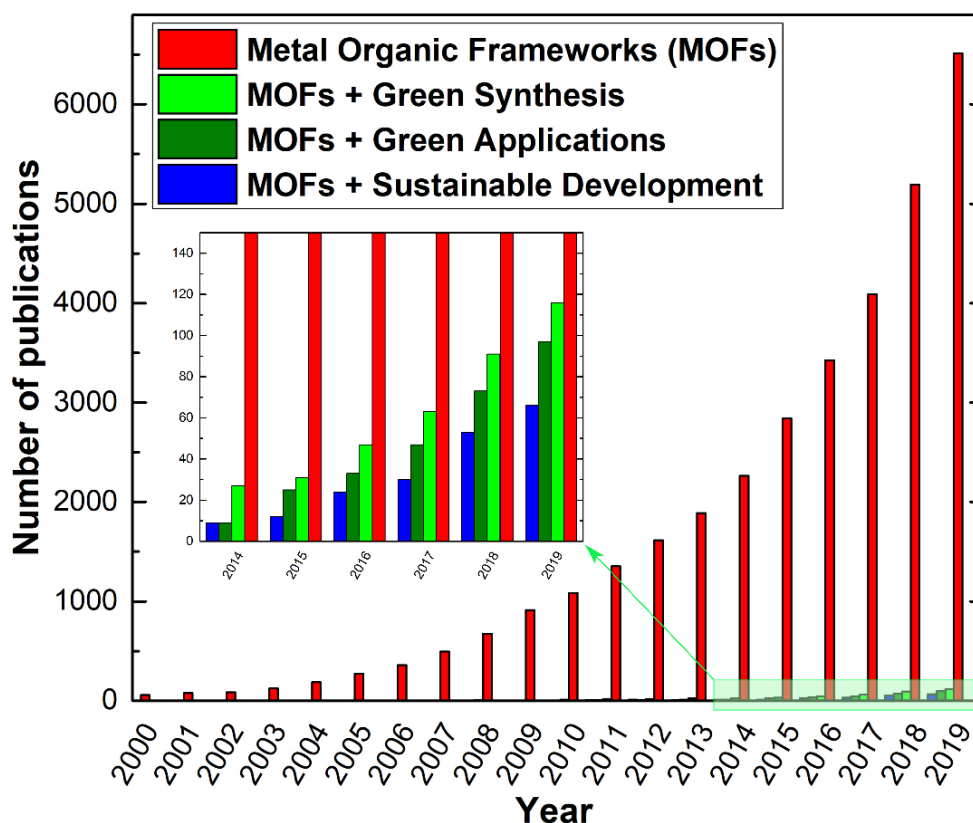
The environment is under great threat because of population growth and the accelerating rate of urbanization. To meet the rising demands for various essential products, rapid industrialization is taking place, which generates increasing amounts of hazardous wastes and toxic gas by-products [1-2]. In order to protect the Earth from these pollutants, the development of new materials for effective and efficient separation of pollutants, as well as the development of green synthesis methods of such materials, are urgently required.

Approximately two decades ago, a new class of crystalline porous materials, Metal Organic Frameworks (MOFs), emerged. MOFs are composed of metal-containing nodes connected with organic linkers by relatively strong chemical bonds [3]. Research into MOFs has seen rapid expansion due to their diverse and easily tunable structures, as well as their wide-ranging potential applications including catalysts, gas separation, gas storage, and carbon dioxide capture [4-5]. Importantly, because of their high surface area and tunable pore sizes, MOFs provide unique opportunities in sustainable development [6], especially in the areas of environmental remediation and energy storage [7-8].

Among many types of MOFs, zeolite-like MOFs, known as zeolitic imidazolate frameworks (ZIFs), are of particular interest in both fundamental research and practical applications. Among ZIF families, ZIF-8 (made of Zn ions and 2-methylimidazolate) is currently the most widely studied ZIF material [9]. ZIF-8 has permanent porosity and relatively high thermal and chemical stability, which makes it an attractive candidate for many applications such as molecular adsorption and separation, and drug delivery [10].

For many years, most of the investigations were dedicated to designing new structures to tailor their properties, without much focus on sustainability. Recently, the need for the commercialization of MOFs and their use in real applications has prompted the development of greener and more scalable/environmentally friendly techniques for MOF syntheses [11]. To achieve this, the principles of green chemistry should be translated into different aspects of MOF syntheses [12]. Equally important is the employment of MOFs in green and sustainable applications whereby providing “clean water and sanitation” and “affordable and clean energy”, two main goals of the Sustainable Development Agenda of the United Nations ([www.un.org](http://www.un.org)) [13].

Figure 1-1 depicts the exponential growth in the number of publications that comprise “metal organic frameworks” in their title, abstract, and keywords, demonstrating the importance of this new class of materials. Figure 1-1 also highlights a substantial research gap in this field; lack of studies on MOFs from the viewpoint of sustainability, as evidenced in the small number of publications which include “green synthesis”, “green application”, and “sustainable development” in addition to “metal organic frameworks” in their title, abstract and keywords.



**Figure 1-1** Number of research publications per year according to Scopus search in July 2020. Keywords: metal organic frameworks, metal organic frameworks green synthesis, metal organic frameworks green applications, metal organic frameworks sustainable development.

To fill this research gap and help realise the goals of the Sustainable Development Agenda, this project aims to develop new green methods to synthesise ZIF nanostructures and to investigate their applications in the areas of water treatment, ion sieving, health security and energy storage. The main novelty of the research lies in the newly developed synthesis methods that are cheap, easy, and ecofriendly for the possible large-scale production of ZIFs. The present thesis also provides a new understanding of the stability of the ZIF structures which plays a vital role in the implementation of their green applications.

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## **Chapter One**

### **Part (II) Literature Review and Research Questions**

#### **1.3 Preamble**

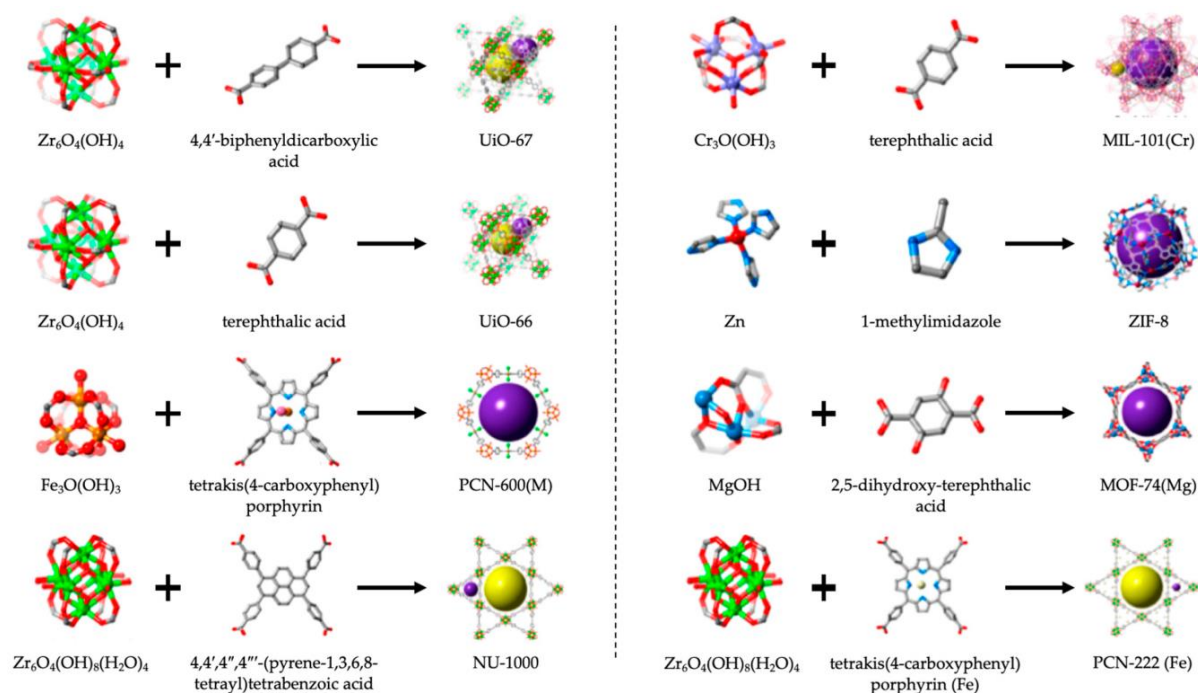
Each experimental chapter (Chapter 2-5) in this thesis is based on publications and thus contains the sections of focused introduction, a specific literature review, and detailed experimental procedures. As such, this chapter gives a general review of the key literature including MOF properties, green synthesis methods, and associated performance that relates directly to the objectives of this thesis.

#### **1.4 Metal Organic Frameworks**

##### **1.4.1 Overview of Metal Organic Frameworks**

Metal Organic Frameworks (MOFs) are crystalline compounds consisting of infinite lattices made of inorganic secondary building units (SBU, metal ions or clusters) and organic linkers, connected by coordination bonds [1–3]. To date, thousands of MOFs are synthesised using various metal clusters and organic ligands. Figure 1-2 shows some of the most common MOFs, along with their metal and organic components [4–6].

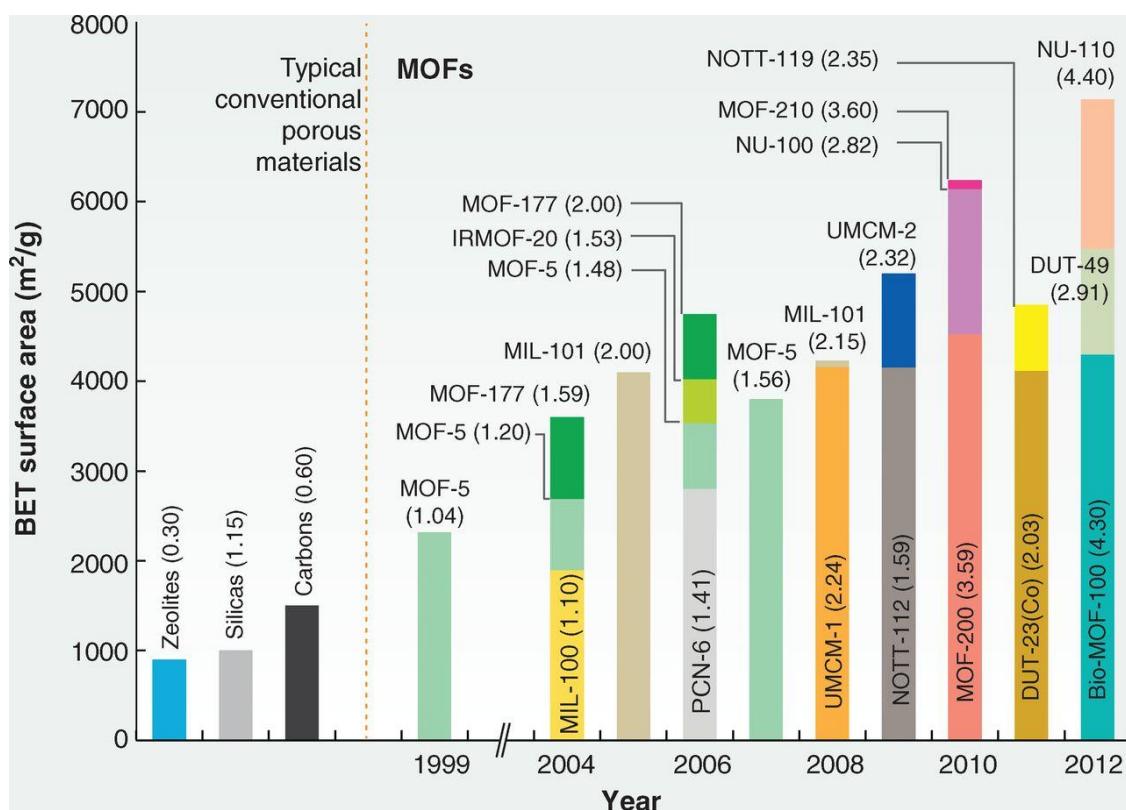




**Figure 1-2 Examples of the metal clusters and organic ligands along with their MOFs structure.**

Reproduced with permission from [5-6]

The crystalline structures of metal-organic frameworks offer ultrahigh porosities along with large pore openings [7]. It is reported that the use of longer ligands results in larger specific surface areas and ultrahigh porosity [4,8]. Figure 1-3 demonstrates examples of the exceptionally large specific surface area of MOFs in comparison to conventional porous zeolites, silicas, and carbons.



**Figure 1-3** Examples of MOFs' specific surface area ( $\text{m}^2 \text{g}^{-1}$ ) and pore volume ( $\text{cm}^3 \text{g}^{-1}$ ) in comparison to conventional porous materials; pore volumes are presented in the parenthesis. Reproduced with permission from [4]

As a unique class of porous materials, MOFs in their numerous different forms are currently used in several technical applications (Figure 1-4). High adsorption capacities and easily tunable pore structures have spurred applications in gas storage, gas separation, drug delivery and molecular sensing [9–15]. Due to the ease of compatibilisation with either organic or inorganic materials, MOFs can form composites with applications varying from (opto)electronic devices and heterogeneous catalysis to food packaging materials and membrane separation [2,16–24]. The inherently high surface area of MOFs provides a notable capacity for the attachment of functional groups and nanoparticles, useful for a variety of applications [25–27].

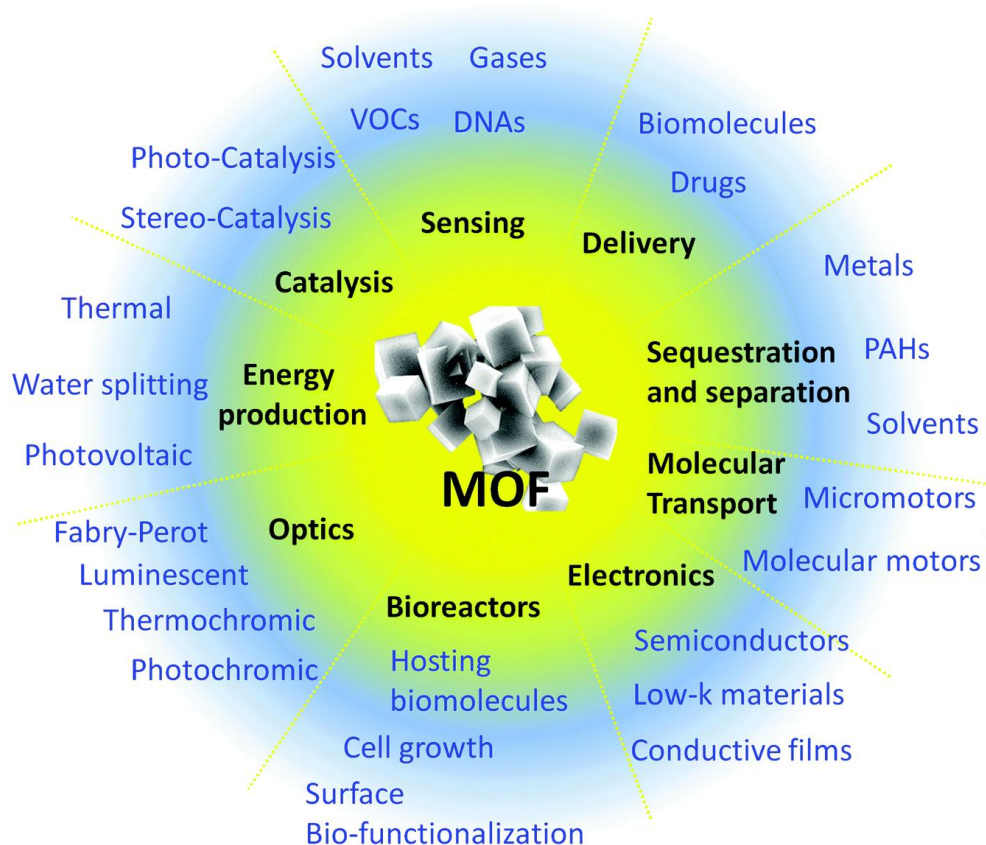


Figure 1-4 Examples of MOFs' applications. Adapted with permission from [28]

The chemical stability of MOFs is of great importance to ensure their functionality during their applications. The chemical stability of MOFs is determined by the strength of metal-ligand bond (thermodynamic stability) and kinetic aspects under the functioning conditions [29]. The principle of hard-soft (Lewis) acids-bases is useful in this respect (Figure 1-5). Carboxylate-based linkers (oxygen-donor ligands) can make strong bonds with high-valent metal ions as hard bases and hard acids, respectively, where the metal cations include  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Zr}^{4+}$ , and  $\text{Ti}^{4+}$ . As for the stable MOFs made of soft bases and soft acids, azolate linkers (nitrogen-donor ligands) and low-valent metal ions (including  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ) are reported to demonstrate good chemical stability [29].

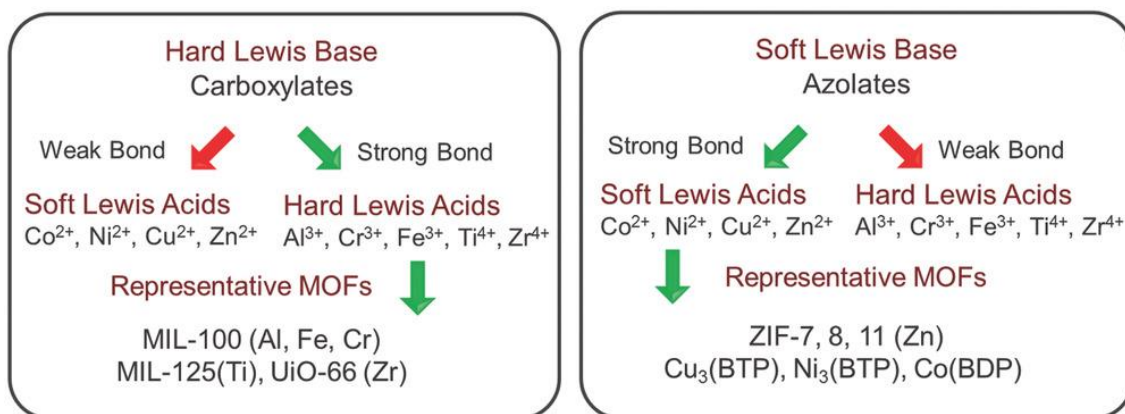


Figure 1-5 Stable MOFs according to hard and soft (Lewis) acids and bases. Reproduced with permission from [29]

## 1.4.2 Zeolitic Imidazolate Frameworks

Zeolitic imidazolate frameworks (ZIFs) are a group of MOFs with 3D structures assembled from tetrahedral metal ions (e.g. Zn, Co) linked by imidazolate anions. Similar to the Si-O-Si bond angle in zeolite structures, the metal-ligand-metal bond angle in ZIFs is close to 145°. Figure 1-6 shows some of the ZIF crystal structures including ZIF-8 (Zn(mIm)<sub>2</sub>, made of Zn cations and 2-methylimidazolate or mIm) [30].

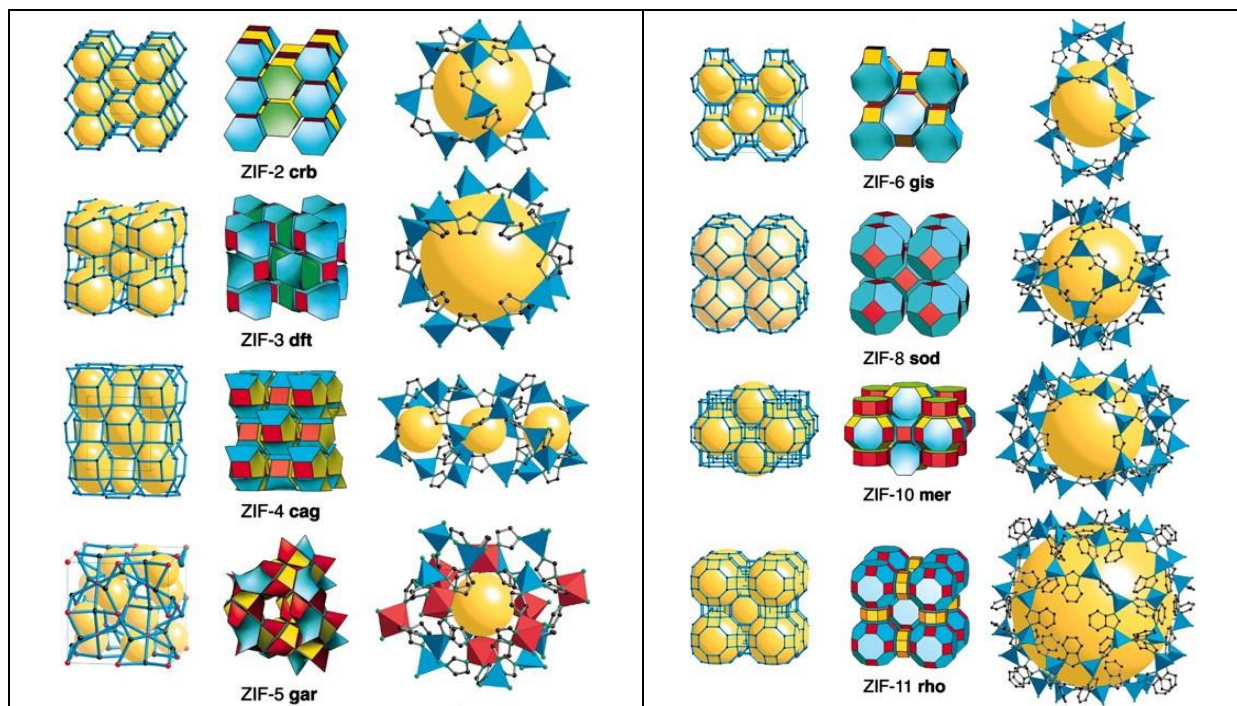
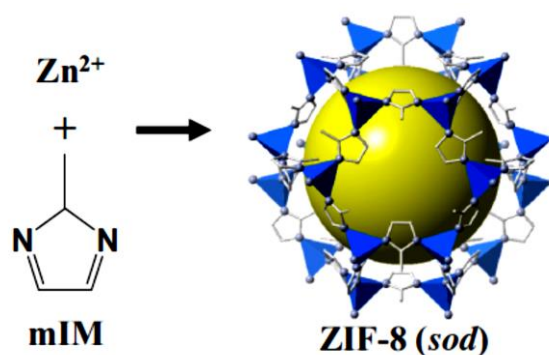


Figure 1-6 Examples of ZIFs' crystal structures; ZnN<sub>4</sub> tetrahedra and InN<sub>6</sub> octahedra are shown in blue and red, respectively and H atoms are not shown. Adapted with permission from [30]



Among the ZIFs, ZIF-8 consists of cages with a diameter of 11.6 Å connected through pore openings of 3.4 Å in diameter (Figure 1-7). ZIF-8 is currently the most widely studied ZIF material for a wide range of applications. ZIF-8 can be synthesised in different forms and particle sizes via several different synthesis methods [30–37]. ZIF-8 powders with average particle sizes from 38 nm to 3 µm [38,39] and different shapes such as rhombic dodecahedral, cubic, octagonal plates, and nanorods [40,41] are reported in the literature. The morphology of ZIF-8 can be tailored by controlling the nucleation and growth rate as well as by directing the preferential growth with, for example, the use of surfactants [42].



**Figure 1-7** Crystal structure of ZIF-8: Zn (polyhedral), N (sphere), and C (line). Reproduced with permission from [35]

Compared with other MOFs, ZIFs exhibit excellent thermal and chemical stabilities [30]. Because of this, many engineering applications such as gas and ion adsorption, gas sensing, gas/solvent separation, and catalysis have been recently proposed for ZIFs utilising their diversity in structure, pore size, and framework functionality [43]. For example, membranes made of ZIFs, in both pure and polymer-mixed matrix forms, have been explored in gas separation applications including hydrogen and carbon dioxide separations (Figure 1-8) and demonstrated promising separation performances [44].

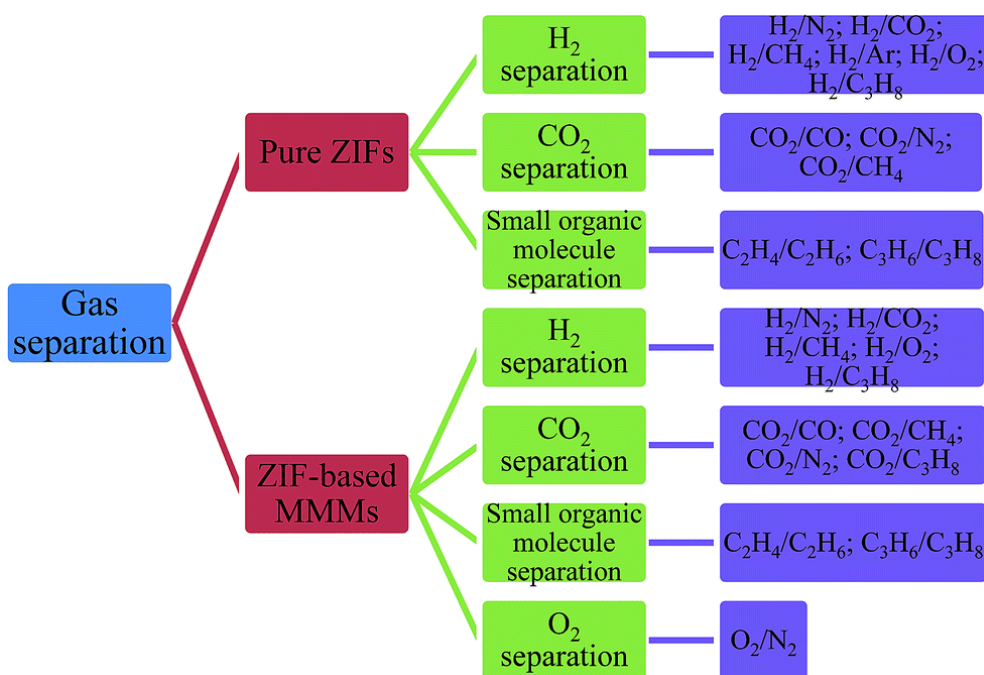


Figure 1-8 Gas separation applications of ZIFs, both in pure and mixed matrix membrane forms.

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It is the semiconducting behaviour upon exposure to light that makes some MOFs useful as photocatalysts [45,46]. Recent research has claimed the suitability of MOFs as photocatalysts, by demonstrating the catalytic degradation of organic pollutants under UV/visible/UV-visible illumination [47–52]. Due to the rich variety of metal-containing nodes and organic bridging linkers, it is possible to construct MOFs with a tuneable light-absorption capacity, thereby engineering desirable photocatalytic properties tailored for individual applications [22,53]. While the potential of using MOFs as photocatalysts for water purification is clearly demonstrated, the research field of photocatalytic MOFs still remains in its infancy, in contrast to the conventional photocatalysts based on metal oxides and sulphides.

MOF-5 is the first MOF that demonstrated photocatalytic behaviour [54]. MOF-5 is composed of  $\text{Zn}_4\text{O}$  clusters located at the corners of the cubic framework structure, connected orthogonally by 1,4-benzendicarboxylic ligands [55]. Some other MOFs that are also constructed with transition metals such as  $\text{Zn(II)}$ ,  $\text{Cu(I)/Cu(II)}$ ,  $\text{Cd(II)}$ ,  $\text{Co(II)/Co(III)}$ , and  $\text{Fe(II)/Fe(III)}$ , were examined as photocatalysts to degrade organic pollutants under UV,

visible or UV-vis light [56]. ZIFs, that consist of tetrahedrally coordinated divalent cations of transition metals ( $\text{Zn}^{2+}$  or  $\text{Co}^{2+}$ ), are a subclass of MOFs for potential photocatalytic applications. The high thermal and chemical stabilities of ZIFs are potentially useful in photocatalytic applications [57–59]. However, controversially, there are some recent reports showing the instability of ZIF structures in the presence of water (i.e. hydrolysis) [60–62]. In order to exploit the potential benefit of ZIFs as new photocatalysts, further investigation on their stability is required.

## **1.5 Green Synthesis of MOFs**

### **1.5.1 Synthesis of MOFs**

Various methods have been developed to manufacture MOFs from different starting materials [63]. Most methods to produce MOFs employ liquid-phase synthesis, where separate solutions of a metal salt and a ligand are mixed together, or a solvent is added to a dry mixture of a solid salt and a ligand in a reaction vial and subsequently heated (Figure 1-9). These conventional preparation methods of MOFs are represented by hydro/solvothermal techniques. Other procedures including mechanochemical synthesis, microwave-assisted synthesis, sonochemical synthesis, and electrochemical synthesis have been utilised to produce MOFs [24,63–65].

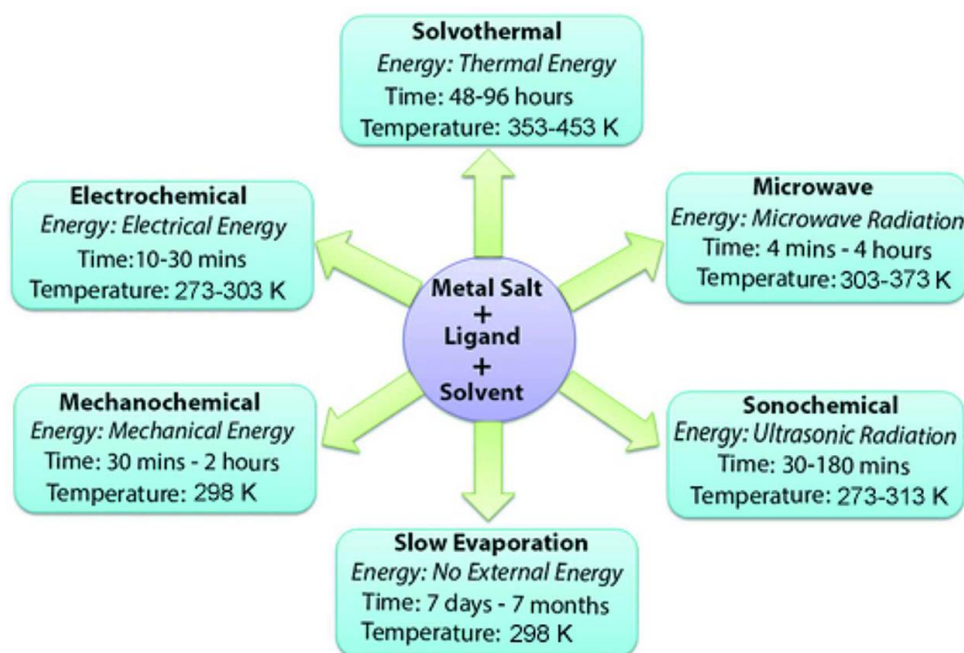


Figure 1-9 Common synthesis conditions of MOFs. Reproduced with permission from [65]

### 1.5.2 Synthesis of ZIFs

Over the past decade, significant research efforts have been made to synthesise ZIFs with different structures and morphologies to explore their unique properties [66]. ZIF-based materials have been conventionally synthesised using hydrothermal/solvothermal techniques in water/organic solvents. Reaction temperatures vary from room temperature up to 200°C and the reaction time spans in the range from minutes to days. These methods involve the use of large amounts of expensive and environmentally unfriendly imidazole ligands and organic solvents such as N,N-dimethylformamide (DMF), N-methylpyrrolidinone (NMP), N,N-diethylformamide (DEF), and methanol [44,66]. In the past years, the synthesis methods for this family of MOFs have developed very rapidly and many new synthesis strategies of ZIFs have been suggested. Both solvent-based procedures and solvent-free routes have been developed for the preparation of ZIF-based materials, which are summarised in Figure 1-10. As can be seen, different synthesis approaches have been adopted in order to produce powder forms or film/membrane structures of ZIF materials [44].



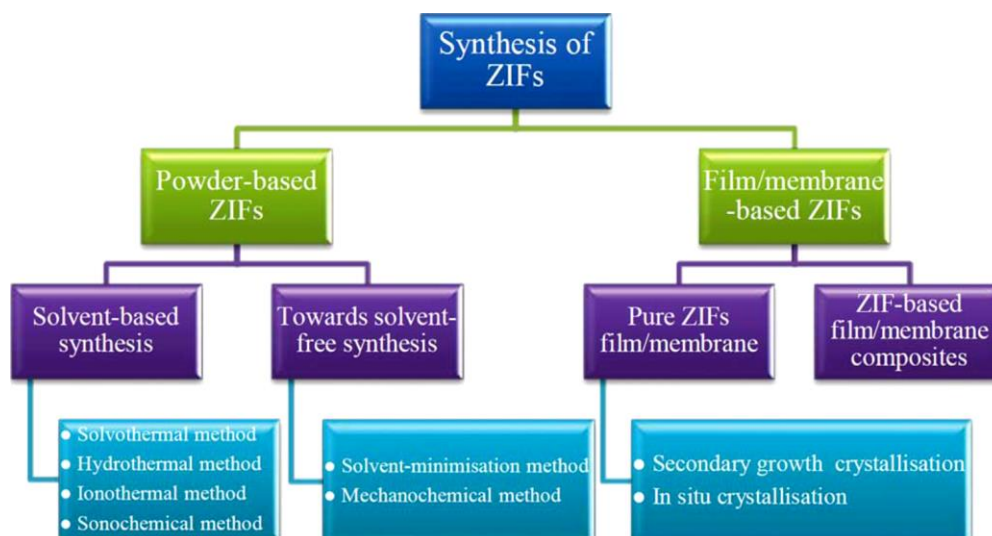


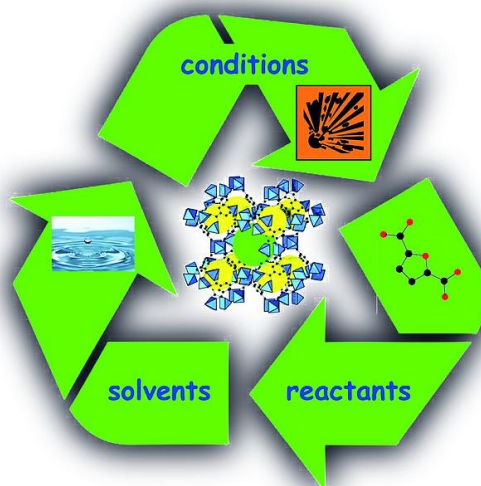
Figure 1-10 Summary of different synthesis methods for ZIF-based materials. Reproduced with permission from [44]

### 1.5.3 Green synthesis

Despite the diversity of the methods developed to synthesise MOFs, most studies on the synthesis of MOFs have been devoted to the optimisation of their properties or improvement of crystallinity or crystal size in order to clarify their crystal structures [67]. There are only a limited number of studies dedicated to the development of green synthesis methods for MOFs. There are several reasons why the study of green synthesis conditions is of great importance. For a large-scale commercial production of MOFs to utilise MOFs in real-life applications, it is essential to use inexpensive, renewable, and environmentally friendly starting materials and to avoid waste while saving energy [68,69]. In another word, the sustainability of the synthesis procedure is crucial to the commercial availability of MOFs.

Figure 1-11 shows three main aspects of MOFs' green and scalable synthesis. Firstly, the amount of solvent used for synthesis and post-synthesis treatment should be minimised. If the solvent-free approach is not possible, water and some organic solvents that can be formed from renewable sources (i.e. ethanol and acetic acid) are the preferred solvents [67,70]. Furthermore, reaction conditions such as temperature, pressure, and time are critical to the green and scalable production of MOFs as they govern the energy consumption and

ease of the manufacturing process [67]. Lastly, the source of metal and organic building-blocks should be renewable and should not generate hazardous by-products upon synthesis reactions. In this regard, the organic linkers acquired from biomass such as fumaric acid and succinic acid are proposed as a renewable source. Also, metal oxides and hydroxides are preferred over nitrates and chlorates which release explosive and corrosive counter anions, respectively [67,69]. Despite the preliminary investigations in this field and documentation of valuable guidelines, the scarcity of the studies on the green synthesis of MOFs represents a significant research gap in the development of MOFs in practical applications. The development of new synthesis techniques may also lead to new MOF structures with outstanding properties [67,71].



**Figure 1-11 Schematic representation of the crucial parameters that define the characteristics of green MOF synthesis. Reproduced with permission from [67]**

Recently, solid raw materials insoluble in solvents, such as metals, metal oxides, and hydroxides, have been utilised for the synthesis of MOFs. For instance, zinc metal and zinc oxide have been employed as solid starting materials instead of dissolved zinc ions from  $\text{ZnCl}_2$ ,  $\text{Zn}(\text{NO}_3)_2$ , and  $\text{Zn}(\text{CH}_3\text{COO})_2$  in solvents [72]. The use of solid insoluble metal sources offers greener reactions and technical benefits comparing to soluble sources of metal ions (Figure 1-12) [72].

In detail, the synthesis of MOFs from a solvent-insoluble solid-phase of raw materials (i.e. metals and metal oxides/hydroxides) has the following advantages, in terms of green-ness of the reactions:

- Raw materials are often cheap, readily available, and suitable for a large-scale production. In contrast, soluble metal salts such as chlorides and nitrates tend to be more expensive.
- When ionic forms of raw materials are utilised in the conventional liquid-based synthesis methods, unwanted salt anions such as  $\text{NO}_3$ ,  $\text{CH}_3\text{COO}$ , and  $\text{Cl}$  coming from the raw materials would result in undesirable wastes/by-products. These wastes or by-products can be avoided by using solvent-insoluble solid forms of raw materials.
- Liquid-based synthesis often requires the use of corrosive raw materials such as chlorides or hazardous, potentially explosive raw materials such as nitrate metal salts.
- Hazardous solvents are typically utilised in solution-based MOF synthesis (e.g., dimethylformamide (DMF), N-methylpyrrolidine (NMP), and dimethyl sulfoxide (DMSO)), which can be avoided or minimised by using solid insoluble metal sources.

The use of solid-phase raw materials also provides the following practical benefits:

- The morphology and microstructure of the solid forms of raw materials can be better engineered through well-established methods (such as sol-gel and atomic layer deposition methods) than soluble raw materials. Solid forms of raw materials can act as a template for directing the growth geometry of MOFs to obtain the desired morphology and microstructure of MOFs [72].

- The amount of metal ions released from solvent-insoluble solid-forms of raw materials can be controlled in different ways (such as changing pH and selective etching), which is not possible using common soluble metal salts in homogeneous solutions. The main driving force for the metal release from the solid raw materials and the subsequent chemical reaction to form MOFs is that MOFs are thermodynamically more stable than the solid form of raw materials in the presence of ligands [72]. This feature allows the creation of unique properties and structures, such as well-defined core-shell structures (precursor-core with MOF-shell) by controlling the release rate of metal ions and crystallisation of MOFs.
- Due to the ability to form complex template structures using solid precursors, the entire design of devices incorporating MOFs (the location, crystal size, orientation, etc.) can be controlled precisely. This is vital to device manufacturing and the performance integrity of the device [28].
- Unique MOF films and membranes can be made from solid raw materials, because the raw materials can be easily deposited on a specific substrate through well-established techniques. These structures are beneficial for gas sensing, gas separation, and membrane applications.
- The use of solid precursor gives ease of combining MOFs with other materials to form complex composite structures. For example, solid precursors can be dispersed in or mixed with host matrices prior to their conversion into MOFs.

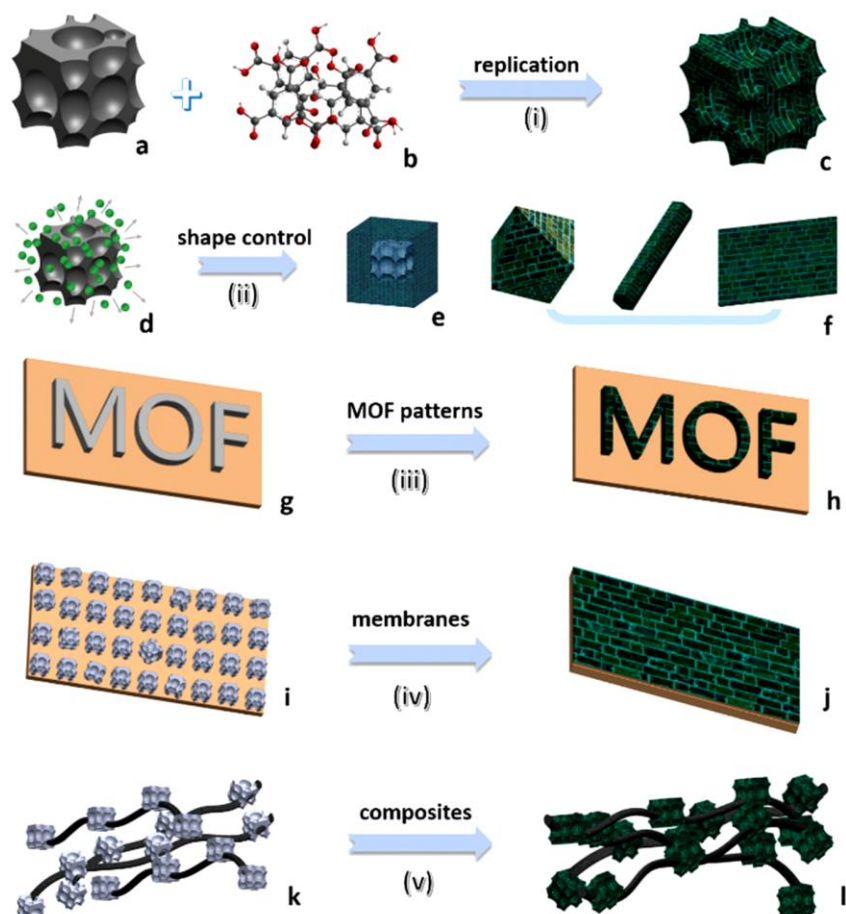


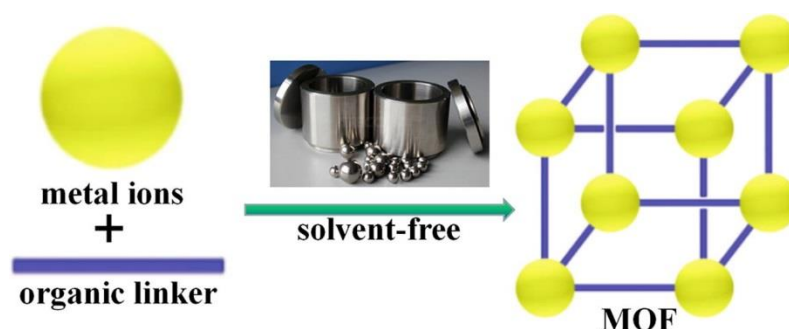
Figure 1-12 Conceptual illustrations summarising various approaches used in the conversion of solid forms of raw materials to MOFs: (a) a solid form of raw material, (b) organic ligands, (c) replicated MOFs, (d) starting materials with releasing metal ions (small green spheres), (e) core-shell structured MOFs, (f) shape-controlled MOFs, (g) raw materials patterns on substrates, (h) MOF assembly on substrates, (i) pre-allocation of raw materials on substrates, (j) MOF membranes or films on the substrate, (k) pristine raw material composites, and (l) MOF-containing composites. Reproduced with permission from [72]

#### 1.5.4 Examples of green synthesis methods

Recently the use of mechanochemistry was demonstrated to produce MOFs from solid raw materials. Mechanochemical processing / ball milling is nowadays widely utilised for the preparation of nanoparticles because of its simple operation and use of relatively inexpensive equipment (Figure 1-13) [67,73]. This process induces solid-state reactions through repeated collisions between the milling balls and reagents [74]. During these collisions, the chemical reactions which usually require high temperatures to occur are initiated at the interfaces of the mixture of reactants at near room temperatures [74]. By controlling the chemical reaction

pathways, milling conditions (e.g. milling ball size, ball-to-powders ratio, and milling time), and proportion of the reagents, nanoparticles with small particle sizes, low agglomeration, and narrow size distributions can be synthesised [75].

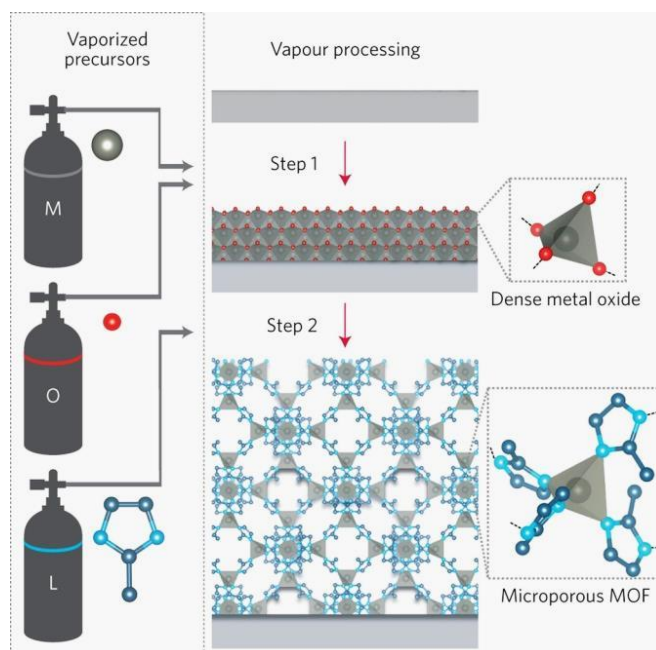
The ability to construct a porous MOF by mechanochemistry was first demonstrated by Pichon *et al.* [76]. Recently, the research group of Friscic [77–80] has developed a promising route to synthesise MOFs by a vigilant control of milling conditions and solvents. The application of mechanochemistry for the construction of metal-ligand bonds can significantly improve the green-ness of the synthesis of porous MOFs, because mechanochemical reactions are independent of the solubility of starting materials (such as metal oxides) and can be designed to be solvent-free (Figure 1-13)[81]. While metal oxides are among the simplest and most inexpensive metal precursors, they are rarely useful in the construction of MOFs using conventional liquid-based techniques due to their low solubility [67,82]. Mechanochemical processing enables the synthesis reactions to occur at near room temperature with quantitative yields while limiting the use of volatile and toxic solvents to minimise the generation of waste [67]. However, the process parameters governing the mechanochemical synthesis of MOFs have not been fully understood.



**Figure 1-13 Solvent-free mechanochemical synthesis of MOFs. Reproduced with permission from [81]**

Vapour phase conversion of metal precursors (e.g. metal oxides) was recently proposed as an alternative method to produce MOF thin films [83] from solid precursors. Ameloot's group showed that zinc oxide thin films (<15 nm) made by atomic layer deposition (ALD) can be transformed to uniform ZIF-8 layers by reacting with 2-methylimidazole vapour at 100°C

(Figure 1-14). In contrast to solvothermal transformation of metal oxides to MOFs, vapour phase conversion provides homogenous nucleation of MOFs where metal ions remain localised during the transformation [83]. This novel approach can also be solvent-free with high atom efficiency (the 2<sup>nd</sup> principle of green chemistry). However, this approach has not been explored to produce MOF films with controlled thickness and porosity.



**Figure 1-14 Chemical vapour conversion of atomic layer deposited metal oxide film (step 1) to MOF film via introducing ligand vapour at an elevated temperature (step 2). Reproduced with permission from [83]**

## 1.6 MOFs for Sustainable Development

The notion of green technologies encompasses many aspects of a product life cycle, including production and application stages. For the MOFs to be utilised in green technologies, research efforts should be dedicated not only to the green synthesis of MOFs but also to the applications of MOFs in sustainable developments [84,85]. These applications include air and water pollution remediation, hydrogen and carbon dioxide capture and storage, solar energy harvesting, and catalytic processes [84]. The structural variety and functionality of MOFs as well as their ability to be utilised as a support or a sacrificial material, have made them interesting candidates to tackle clean energy challenges [86,87].



Figure 1-15 displays the milestones in clean/green energy applications of MOFs and their composites and derivatives, starting from MOF for methane storage in 2002 to MOF-derived catalysts for water splitting in 2019 [88]. Applications of MOFs in clean energy technologies include hydrogen energy (as absorbents, supports for chemical storage, and catalysts/photocatalysts for hydrogen generation from water), fuel cells (as electrolytes, electrode catalysts, and catalyst precursors), lithium-ion batteries (as electrode materials and materials precursors), supercapacitors (as electrode materials and materials precursors), and solar cell (as semiconductors) [86]. Despite the advancement of this research field, the use of MOFs in energy applications is still limited due to their low chemical stability and low electrical conductivity [88]. Although MOF-derived carbonaceous nanostructures exhibit exceptional chemical and electrical stabilities, their production requires high-temperature pyrolysis processes that is difficult to control over the microstructures, which raises concerns about the economic feasibility and practicality of such materials [88].

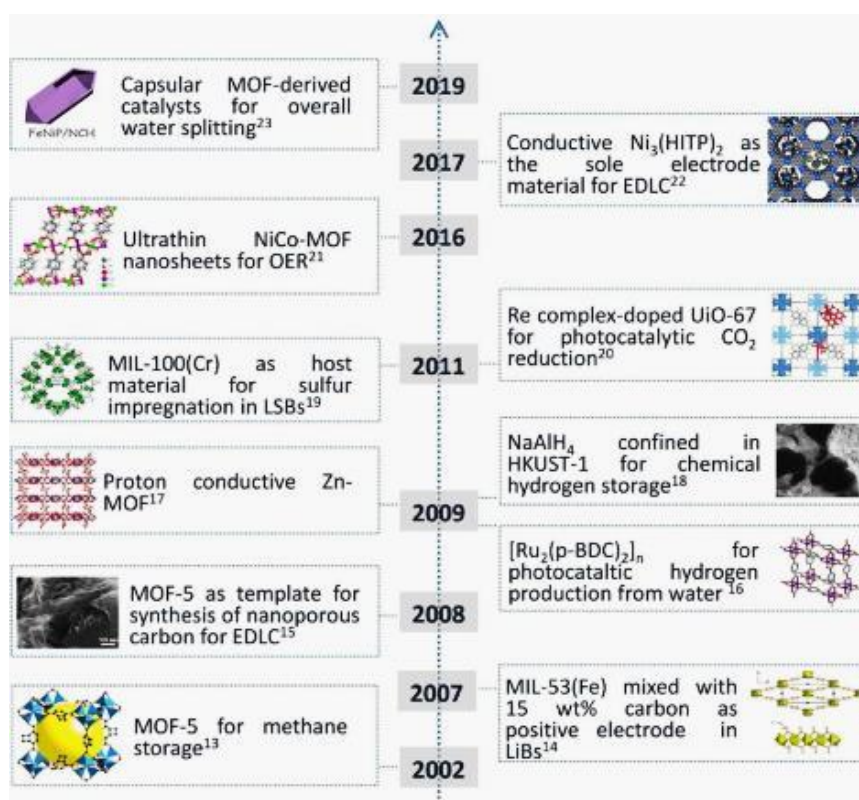


Figure 1-15 Milestones of MOFs' applications in clean/green energy. Reproduced with permission from [88]



Another important application field in sustainable development is water security. Access to clean water and purification of aquatic systems are of great importance to our society and environment. Due to the uniform porous structures with adjustable pore sizes and functionalities, MOFs have presented excellent potential to achieve this goal through the removal of contaminants from water [50,89,90]. MOFs such as ZIF, MIL (Matériaux de l'Institut Lavoisier), and UiO (University of Oslo) families have been employed to adsorb inorganic contaminants (such as toxic metal cations and nuclear wastes) and organic pollutants (pharmaceutical products and organic dyes) from water [90].

Despite the research progress in these application fields, controversial reports on the instability of MOF structures in the presence of water have hindered further development of their applications in aqueous media.

## 1.7 Water Stability of MOFs

The structural and chemical stability of MOFs in the presence of water molecules is critical to water-related applications such as adsorption (gases, organic molecules, and ions), membrane separation (gas separation, pervaporation, and liquid filtration), sensing (water detection and detection in presence of water), catalysis (water as a reaction source or solvent/by-product), proton conduction, photocatalytic water treatment, water splitting, and biological application [23,29]. Since water or moisture may be present in most of the production, storage, and application stages of MOFs, it is critical to assess the water stability of MOFs.

As previously mentioned, thermodynamic principles and knowledge on bond strength can be used to predict the stability of MOFs. The mechanism of MOFs' degradation in the presence of water (Figure 1-16a) is the substitution of the organic linker with hydroxide or water [91,92]. As such, stronger coordination bonds (hard Lewis acids and bases, or soft Lewis acids and bases) between metal sites and organic ligands lead to more stable MOFs [29]. In

addition, the presence of hydroxide and proton ions in water (i.e. bases and acids, respectively) leads to different stability of MOFs.

Figure 1-16b displays the possible decomposition reactions of thermodynamically “water-stable” MOFs (hard Lewis acids and bases, or soft Lewis acids and bases) in acids and bases [29]. For example, PCN-222 (made of zirconium cations and carboxylate ligands) is reported to exhibit excellent stability in concentrated acids (e.g. HCl); however, it degrades in diluted bases [93,94]. This is due to the lower affinity of protons to replace high valency Zr ions in acidic conditions and the higher affinity of hydroxides to bind to metal ions (replacing the ligand) in alkaline conditions [29].

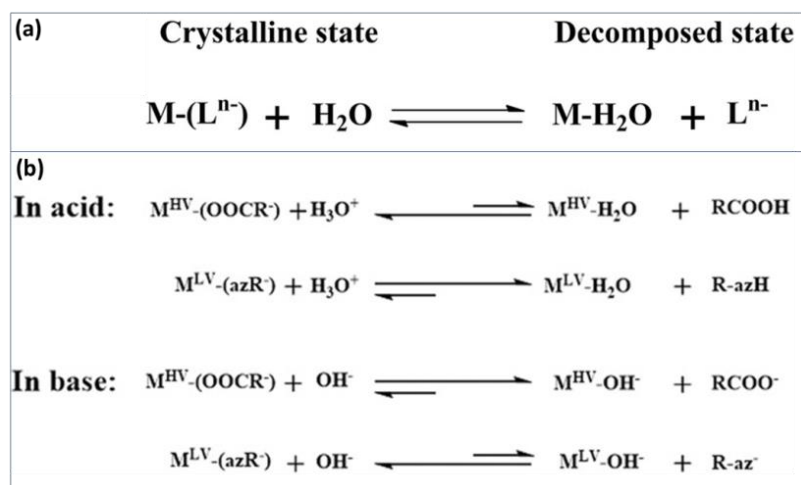


Figure 1-16 Decomposition mechanisms of MOFs in (a) water, and (b) aqueous acid/base;  $M^{HV}/M^{LV}$ : high/low-valency metal ions; RCOOH: carboxylate- based ligand; RazH: azolate-based ligand.

Reproduced with permission from [29]

Regardless of the thermodynamic predictions, different experimental conditions including particle sizes and crystal defects along with limited characterization techniques can lead to controversial observations [29]. Thus, it is essential to study the stability of MOFs experimentally.

ZIF-8 is known as one of the most thermodynamically water-stable MOFs [95]. The common experimental method to study the stability of MOFs is by comparing their X-ray diffraction (XRD) patterns, Brunauer–Emmett–Teller (BET) surface areas, and electron microscopy,

before and after the exposure to water [29]. The water stability of ZIF-8 has been experimentally demonstrated in many reports, mainly using these methods [30,92,96–98]. Different analytical tests such as inductively coupled plasma atomic emission spectroscopy (ICP-AES) to trace the released metal ions [62] and time-resolved atomic force microscopy (AFM) to monitor the MOFs' morphology [99] are also proposed to study the stability of ZIFs in water. However, some of these analytical techniques are not sufficiently sensitive to quantitatively probe the hydrolysis, or not useful tools to analyse the water stability of MOFs, as presented in detail in this thesis. For example, the use of ICP-AES to trace the concentration of released metal cations in filtrate can be deceiving if the cations precipitate out during the powder filtration. In addition, recent studies documented some evidence of hydrolysis by varying the testing conditions such as long exposure to water (three months) [100], hydrothermal conditions (80°C) [101], and methods for powder collection after immersion tests [61,102].

There are ions commonly present in aqueous applications such as phosphates and carbonates that can be destructive to MOF structures. Thus, the robustness of the MOFs should be examined in aqueous solutions of these salts (e.g.  $K_3PO_4$ , and  $Na_2CO_3$ ) [29,103,104]. However, the considerations towards the effects of such ions have been largely ignored in the past.

Despite the research progress in synthesising water-stable MOFs, the extent of MOFs' stability in various aqueous environments is not well understood and the methods to study the instability of ZIFs in water have not been established.

## 1.8 Significance, Research Questions, and Novelties

ZIFs have captured significant interest in the last decade due to their high surface area and relatively high thermal and chemical stability. This remarkable family of MOFs provides unique opportunities in sustainable applications such as environmental remediation and

energy storage. However, the research on ZIFs is still at an early stage. In particular, further studies are urgently required in the following areas to developing real-world applications of ZIFs: (1) green synthesis routes, (2) sustainable applications, and (3) the water stability of ZIFs. Real-world applications of ZIFs require a large-scale production through environmentally friendly synthesis routes. The applications of ZIFs in addressing sustainable development challenges and their chemical stability in presence of water are still underdeveloped.

In these research areas, the literature review identified the following research gaps:

- For the **green synthesis** of MOFs, it is not desirable to employ volatile and toxic solvents along with explosive/corrosive metal precursors. To address this issue, green synthesis of MOFs via novel synthesis methods (using metal oxide/hydroxide precursors) such as mechanochemical processing (MCP) and chemical vapour conversion (CVC) techniques has been proposed in the past. However, the process parameters governing the synthesis of MOF powders/films via these techniques have not been fully understood.
- MOFs have been used in many **sustainable applications** such as air and water pollution remediation, hydrogen and carbon dioxide capture and storage, solar energy harvesting, and catalytic processes. However, there are still several challenges in developing new ways of utilising MOFs for these applications. The challenges include modifying the surface chemistry of MOF nanoparticles, tuning the extrinsic porosity of MOF films, and quantifying the chemical stability of MOFs in different media.
- Furthermore, the **chemical stabilities** of MOFs in different aqueous environments are not well characterised as evidenced by the contradictory observations reported in the literature. In addition, the methods to analyse the water stability of MOFs have not been established.

In order to fill the above research gaps, the present investigation formulated the following specific research questions, by focusing on the ZIF-family of MOFs:

- What synthesis conditions should be satisfied to minimise the waste generation and environmental impacts of ZIF production, using MCP and CVC techniques?
- What are the unique features of ZIFs that are synthesised using green methods, what sustainable applications can exploit the unique features, and how can the unique features be tailored using the green synthesis methods?
- What are the best practices to investigate the stability of ZIFs in different environments, what are the factors influencing the water stability of ZIFs, and what are the implications of the stability for the green/sustainable applications?

The scope of this work is limited to the ZIF family, primarily ZIF-8. However, the knowledge acquired in this thesis may be generalised into the synthesis, stability, and application of other members of MOF family.

## 1.9 Thesis Structure

To address the research gaps/questions, this thesis is structured with the following chapters. It should be noted that each experimental chapter (Chapter 2-5) has a focused introduction/literature review section along with detailed experimental procedures.

- **Chapter 2:** This chapter investigates a green and scalable synthesis method to produce well-dispersed ZIF-8 nanopowders (ca 80 nm) with a high yield and minimal waste. It is demonstrated that mechanochemically synthesised ZIF-8 nanopowders with little agglomeration have higher efficacy in adsorbing organic pollutants than ZIF-8 nanopowders synthesised via common solution-based methods, due to their unique surface characteristics.

- **Chapter 3:** This chapter presents a solvent-free methodology for the three-dimensional structuring of MOFs in monolithic films with tunable extrinsic porosity. The hierarchically porous structures of ZIF-8 films were engineered via the vapour-phase conversion of metal oxide precursors. The use of dense and crack-free ZIF-8 monoliths as molecular sieve ion separators in a model lithium-sulphur battery system resulted in a significant increase in the long-term stability and performance of the battery system over other benchmark separators.
- **Chapter 4:** In this chapter, the water stability of ZIFs is studied using a new combination of analytical tools. The study reveals that, in contrast to the reported excellent structural stability of ZIFs in water, ZIF-8 undergoes hydrolysis in water. This study demonstrates the importance of analysing both filtered powders and the filtrate liquid systematically, in particular by using UV-Vis spectroscopy and thermogravimetric analysis. The combination of analytical tools enabled the quantitative study on the effects of ZIF concentrations in water, cobalt doping levels, and amounts of ligands in water on the water stability of ZIF samples.
- **Chapter 5:** In this chapter, the instability of ZIF-8 and release of ZIFs' building blocks (i.e.  $\text{Zn}^{2+}$  and  $\text{mlm}^{-1}$ ) in antibacterial media are studied. It is demonstrated that the antibacterial properties of ZIF-8 against gram-negative *Escherichia coli* (*E. coli*) is superior to ZnO. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) and UV-Vis absorption spectroscopy revealed that the degradation of ZIF-8 in the culture media is enhanced by the reaction of released  $\text{Zn}^{2+}$  with phosphate ions in PBS, or with organic moieties in LB broth. As an extension of this study, the use of ZIF-8 to supplement the bacteriostatic properties of superhydrophobic surfaces (SHSs) is also presented in the second part of this chapter. Sub-micron size ZIF-8 particles were incorporated in SHSs and the changes in superhydrophobicity and antibacterial properties of the surface are analysed. The addition of ZIF-8 particles

(up to 15 wt%) to the SHSs imparted dual functionality in the coating, by introducing bactericidal properties while maintaining the superhydrophobicity.

- **Chapter 6:** This chapter presents a summary of the findings, the key contributions of the work to the research field, and a brief discussion of the future work.

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## Chapter Two

### Green full conversion of ZnO nanopowders to well-dispersed ZIF-8 nanopowders via a stoichiometric mechanochemical reaction for fast dye adsorption

#### 2.1 Preamble

The publication relevant to this chapter is “M. Taheri, I. Bernardo Di, A. Lowe, D. Nisbet, T. Tsuzuki, Green full conversion of ZnO nanopowders to well-dispersed zeolitic imidazolate framework-8 (ZIF-8) nanopowders via a stoichiometric mechanochemical reaction for fast dye adsorption, *Crystal Growth & Design*, Vol. 20 (4), 2020, pp 2761-2773.” The relevant supporting information is presented in Section 2.8.

#### 2.2 Abstract

In recent years, many nanofabrication methodologies to engineer metal organic frameworks (MOFs) have been investigated. However, there are only a small number of studies that explore scalable and environmentally friendly synthesis routes. This study reports the production of well-dispersed MOF nanopowders from an inexpensive precursor, in a green and scalable manner, with a high yield and minimal waste, for water remediation applications. One-step mechanochemical processing of a stoichiometric ratio of ZnO nanoparticles and 2-methylimidazole resulted in the full conversion of ZnO nanopowders into zeolitic imidazolate framework-8 (ZIF-8) of ca 80 nm in diameter with little agglomeration. The particles had a surface area of  $1,885 \text{ m}^2 \text{ g}^{-1}$ , among the highest reported for ZIF-8 and close to the theoretical maximum of  $1,947 \text{ m}^2 \text{ g}^{-1}$ . For the first time, this study presents an enhanced ability of the converted nanopowders to adsorb more model organic pollutants than ZIF-8 nanopowders synthesised via the most commonly used solution-based method. Details of the processing conditions including milling-ball size, milling time, and post-milling treatment that influence the conversion yield, were systematically investigated using dry

reactive grinding and liquid assisted grinding. This work provides a new strategy for the commercial production of wide-ranging MOFs for environmental applications.

## 2.3 Introduction

In recent years, metal organic frameworks (MOFs), a class of meso- and micro- porous organic-inorganic hybrid materials, have been extensively investigated for a variety of applications [1–6]. A large number of different MOF materials have been synthesised and their unique properties have been broadly exploited [7,8]. One group of MOFs with relatively high thermal and chemical stability are zeolitic imidazolate frameworks (ZIFs) that consist of tetrahedral metal ions connected with imidazolate molecules [9]. Among them, ZIF-8, made of Zn ions and 2-methylimidazolate, is currently one of the most widely studied ZIF structures for a number of applications including water purification [10], CO<sub>2</sub> capture [11], gas sensing [12], and drug delivery [13,14].

Although many nanofabrication methodologies to engineer MOFs have been explored, most of these studies focused on the optimization of MOF's properties or on the clarification of their crystal structures. There are only a small number of studies that explore scalable and environmentally friendly synthesis routes, which are critical to their commercial translation [15–18]. In fact, it is still a considerable challenge to produce well-dispersed MOF nanoparticles using a scalable and green method without generating much wastage [19,20]. For example, Feng *et al.* synthesised well-dispersed ZIF-67 and ZIF-8 nanoparticles of less than 100 nm in diameter, but hazardous dimethyl sulfoxide as a solvent and a large quantity of excess ligand were used [21]. Marrett *et al.* demonstrated the use of supercritical CO<sub>2</sub> for clean and scalable production of ZIF-8, but the end product was hard aggregates and an excess amount of ligands, instead of a stoichiometric amount, was required to obtain pure ZIF-8, resulted in the wastage of the raw material [18]. Crowford *et al.* reported a continuous large-scale production of MOFs using an extrusion technique that allowed the operation



without using solvents, but a large quantity of excess ligand was required to complete the reaction [22]. The syntheses of ZIF-8 [23] and UiO-66-CO<sub>2</sub>H [24] in water, instead of organic solvents, were reported as environmentally friendly processes, but the method required excess amounts of ligands, which sacrifices the reactant efficiency [19]. Several attempts have also been made to minimise the wastage of raw materials in the solvent-based syntheses of MOFs, by recycling the mother liquors while maintaining the crystallinity and specific surface area of resulting MOFs [25–27].

This chapter investigates a method to synthesise well-dispersed ZIF nanoparticles wherein the method is scalable and uses inexpensive, renewable and environmentally friendly starting materials, whilst concomitantly avoiding waste and saving energy. To achieve this, the versatile nature of reactive ball-milling is exploited. Mechanochemical processing, or reactive ball milling, is nowadays widely utilised for the preparation of nanoparticles, due to its inherent ease of operation and the use of relatively inexpensive equipment [8,28,29]. Mechanochemical processing is advantageous as a scalable nanofabrication method, as it allows faster reactions at near-room temperature with quantitative yields. It also minimises the use of solvents during production and thus reduces the issues associated with waste disposal [8,22]. Mechanochemical processing has been demonstrated as a green and sustainable method for the commercial-scale production of a variety of nanomaterials [30,31].

In the past, mechanochemistry was utilised to construct porous MOF, where vigilant control over the milling conditions and solvents is shown to dictate the final properties and hierarchical nanostructure [32–38]. In addition, it was shown that mechanical energy input into the raw materials can induce surface activation and local short-range heating, allowing the synthesis of high-entropy MOFs which cannot be formed via conventional solvent-based methods [39]. Here, these studies are extended by probing the process parameters

governing the mechanochemical synthesis of MOFs, exploiting them to ensure that scalable, safe, and green synthesis is achieved.

A distinct advantage of using mechanochemical processing for MOF synthesis is that mechanochemical reactions can be tailored to not require the starting materials to be soluble in a liquid phase. The employment of volatile and toxic solvents during the nanofabrication is not desirable for many applications of MOFs including water purification or drug delivery, due to associated health and environmental concerns. The application of mechanochemistry for the construction of metal-ligand bonds can provide a unique synthesis path, alternative to solution-based methods. However, it is still challenging to obtain well-dispersed particles with a narrow particle size distribution by using solvent-free approaches [18,40].

Another feature of mechanochemical synthesis is the size- and shape- uniformity and smallness of resulting nanoparticles [41,42]. During recent years, the capability of ZIF-8 to remove water contaminants such as heavy metals, organic dyes, and pharmaceuticals has been studied through adsorption of large molecules and small ions on the external and internal surface of ZIF-8, respectively [43–50]. Hence, synthesising well-dispersed ZIF-8 nanoparticles with higher external surface areas, which mechanochemical processing can offer, is of great importance to their environmental applications [10,51,52].

Another advantage of mechanochemical processing is the use of simple reactants, such as metal oxides, to form MOFs. Metal oxides such as ZnO are among the simplest and most inexpensive metal precursors. The advantage of using metal oxide/hydroxide starting materials in comparison with metal salts is that the by-product of the reaction is water, and there is no need to use organic solvents, additives, or additional extra ligand [18,53,54]. However, metal oxides are rarely useful in the construction of MOFs materials using solution-based methods, due to their low solubility [8,55].

Although there are a few reports on the mechanochemical conversion of ZnO to ZIF-8 [18,56–62], it has been proved challenging to achieve the full conversion of a metal oxide to the well-dispersed MOF without using excess ligands, highlighting the significant novelty and potential impact of the methodology reported herein. For instance, Beldon *et al.* reported a detailed study on the use of mechanochemistry to produce ZIF-8 from ZnO [63]. In their report, a stoichiometric mixture of ZnO (80 mg) and 2-methylimidazole (164 mg) was mechanochemically processed in the presence of different grinding liquids (ethanol, N,N-dimethylformamide or N,N-diethylformamide), and the addition of salts were employed to ensure the conversion of ZnO to ZIF-8 [63]. However, in this landmark study, the conversion rate was not reported despite its critical importance to commercial production. More recently, dry mechanochemical conversion of ZnO to ZIF-8 has been reported by Tanaka *et al.* [64], wherein the conversion rate after 96 hours of milling was 80% with a Brunauer-Emmett-Teller (BET) specific surface area of  $1,480 \text{ m}^2 \text{ g}^{-1}$ . Increasing the milling time to 240 hours resulted in minimal improvement in conversion rate (82%), but a lower BET specific surface area of  $1,180 \text{ m}^2 \text{ g}^{-1}$ . Later in 2018, they reported a catalytic effect of 10 mol% zinc acetate on the conversion rate of ZnO to ZIF-8 in a salt-assisted mechano-synthesis process, where almost 100% conversion was achieved in 3 hours [40]. However, the resulting particles are highly agglomerated. Marrett *et al.* used pre-milled ZnO and 2-methylimidazole under supercritical  $\text{CO}_2$  conditions to produce ZIF-8 but a minimum 10 mol% excess amount of ligand was required to avoid the formation of undesired zinc 2-methylimidazole carbonate phase [18].

Considering these, a new mechanochemical route is developed to fully convert ZnO into well-dispersed ZIF-8 nanoparticles without using excess ligand, yielding smaller particle sizes (*ca* <100 nm) and higher surface areas (*ca* > $1,880 \text{ m}^2 \text{ g}^{-1}$ ) compared with the most commonly used solution-based syntheses routes. Significantly, this nanomorphology resulted in improved efficacy in the adsorption of organic pollutants. To report this

inexpensive, scalable, and green methodology, the synthesis parameters such as milling time and post-milling treatments are systematically studied.

## 2.4 Experimental

### 2.4.1 ZnO nanopowder starting material

One of the raw materials, ZnO nanoparticles, was mechanochemically synthesised following the previously reported procedure [65]. Briefly, 10.6 g of a stoichiometric mixture of the starting powders, corresponding to the reaction equation of  $\text{ZnCl}_2 + \text{Na}_2\text{CO}_3 + 8.6\text{NaCl} \rightarrow 3\text{ZnCO}_3 + 10.6\text{NaCl}$ , was milled for 4 hours in a Spex 8000 mixer/mill and subsequently heat-treated in air at 400 °C for 30 minutes to decompose  $\text{ZnCO}_3$  nanoparticles into ZnO. All reagents were commercially available and used as received without further purification. The NaCl diluent phase was placed in the starting powder mixture so that the volume ratio of  $\text{ZnCO}_3$  : NaCl in the product phase becomes 1 : 10 to ensure a low agglomeration-degree of ZnO nanoparticles. The NaCl phase was removed by washing the resulting powder with 50 mL of deionised (DI) water using a centrifuge and an ultrasonic bath, until the salinity level of the supernatant became less than 50 ppm.

The mechanochemically synthesised ZnO nanoparticles used in this chapter had a specific surface area of  $43.6 \text{ m}^2 \text{ g}^{-1}$ . This specific surface area is equivalent to an average particle size of 24.5 nm, which was in good agreement with the results of DLS analysis and electron microscopy (Figure S 2-1). The starting ZnO nanoparticles had a wurtzite crystal structure (Figure S 2-1).

### 2.4.2 Synthesis of ZIF-8

Mechanochemical synthesis of ZIF-8,  $\text{Zn}(\text{mIm})_2$ , was performed with a Spex 8000 mixer/mill using a ball-to-powder mass ratio of 10:1. The stoichiometric mixture (1.7 g) of ZnO

nanopowders and 2-methylimidazole (HmIm, Sigma-Aldrich), corresponding to the reaction equation of  $\text{ZnO} + 2\text{HmIm} \rightarrow \text{Zn(mIm)}_2 + \text{H}_2\text{O}$ , was sealed in an 80 mL stainless steel vial along with stainless steel balls with diameters of 6.7, 9.5 and 12.5 mm. The powder mixture was milled for up to 12 hours. For liquid-assisted grinding, methanol was added to the mixture in the ratio of  $1 \mu\text{L mg}^{-1}$  prior to milling. Removal of unreacted HmIm was carried out by repeatedly washing the milled powder with 50 mL of DI water or ethanol, using a centrifuge (10 min) and an ultrasonic bath (one min). After three washes, samples were dried at 60 °C overnight. Alternatively, heat treatment for 2 hours was carried out on the as-milled powders at 120, 150, and 180 °C, to remove the unreacted HmIm.

For the dye-adsorption study, ZIF-8 powders produced using a methanol-based method, were also studied. For this, zinc acetate dihydrate (1 mmol) and 2-methylimidazole (8 mmol) were separately dissolved in 15 mL of methanol at room temperature. Then, the zinc solution was added to the ligand solution while being stirred by a magnetic stirrer. After one hour of stirring at room temperature, the powders were collected and washed three times with methanol. Subsequently, the ZIF powders were dried at 60°C overnight. In order to obtain nano-scale ZIF-8 using this method, a  $\text{Zn}^{2+}:\text{HmIm}:\text{CH}_3\text{OH}$  molar ratio of 1:8:600 was used, which resulted in the wastage of HmIm and the use of a large quantity of the organic solvent per mole of ZIF-8.

### 2.4.3 Characterisation of ZnO nanoparticles and ZIF-8

Powder X-ray diffraction (PXRD) patterns were obtained using a D2 Phaser with a Cu-K $\alpha$  radiation source (Bruker, USA). Average crystallite sizes were estimated using the Scherrer equation. The morphology and microstructure of the nanopowders were analysed by scanning electron microscopy (SEM, Zeiss UltraPlus FESEM, Germany) and transmission electron microscopy (TEM, JEOL 2100F FEGTEM, Japan) with an accelerating voltage of 2 and 200 kV, respectively. Prior to SEM analysis, samples were sputter-coated with platinum for 90 sec at 15 mA. Thermogravimetric analysis (TGA) was carried out on ca 20 mg of

nanopowders using a STA8000 instrument (PerkinElmer, USA) in air using alumina crucibles. Specific surface areas of the specimens were measured from nitrogen adsorption isotherms at liquid nitrogen temperature using a Tristar II 3020 (Micromeritics, USA). Prior to the surface area analysis, samples were degassed at 120 °C for 24 hours under vacuum. Brunauer–Emmett–Teller models ( $S_{\text{BET}}$ ) and Langmuir models ( $S_{\text{L}}$ ) were applied to calculate the apparent surface area from adsorption data. The pressure range used was between 0.23 and 60 mmHg for  $S_{\text{L}}$ , and  $p/p_0$  between 0.001 and 0.05 for  $S_{\text{BET}}$ , where  $P_0$  is ~715 mmHg. Dynamic light scattering (DLS) and zeta potential measurements were used to characterise the size distribution and surface charge of nanopowders using a Zetasizer Nano-S (Malvern Instruments, UK). All measurements were carried out at room temperature. At least 3 replicates were measured to ensure the repeatability of the results. X-ray photoelectron spectroscopy (XPS) data were acquired with a Nexsa Surface Analysis System (ThermoFisher, USA) equipped with a flood gun for charge neutralization. The spectra were acquired with a monochromated Al  $k_{\alpha}$  X-ray gun with a spot size of 400  $\mu\text{m}$ , and the pass energy was set at 20 eV for the high-resolution spectra and at 50 eV for the survey spectra.

It is noteworthy to mention that the optimised synthesis method to convert ZnO into well-dispersed ZIF-8 nanoparticles was repeated at least three times. Characterizations of the samples (XRD and SEM analyses) showed the high reproducibility of the synthesis method.

#### 2.4.4 Dye adsorption

To investigate the dye adsorption performance of the ZIF-8 nanopowders, stock solutions of model organic dyes (Rhodamine B and methylene blue) were prepared and diluted with DI water to obtain the desired concentration of the contaminants. ZIF-8 powders (25 mg) were ultrasonically dispersed in DI water (50 mL). The dispersed ZIF-8 suspensions were added to 50 mL of dye solutions with a concentration of 10 ppm while stirring. This results in the presence of 25 mg of the adsorbent in 100 mL of 5 ppm dye solution. The experiments were carried out in the dark to avoid photolysis. At different intervals up to 2 hours, 5 mL of sample

suspensions were collected and filtered using a 0.20  $\mu\text{m}$  syringe filter. A Cary 60 UV-Vis spectrophotometer (Agilent, USA) was utilised to analyse the concentration of Rhodamine B (RhB) and methylene blue (MB) by monitoring their characteristic absorbance peaks at 555 nm and 664 nm, respectively.

## 2.5 Results and discussion

### 2.5.1 Dry milling

To investigate the effect of milling-ball size on the dry conversion of ZnO nanoparticles to ZIF-8, stainless steel balls with diameters of 6.7 (16 balls), 9.5 (4 balls), and 12.5 mm (2 balls) were chosen, and the mixtures were milled for 2 hours. The XRD and TGA results (Figure S 2-2) revealed that 9.5 mm balls resulted in the most efficient conversion of ZnO. The specific surface area of the sample milled with 9.5 mm balls was higher than that milled with larger or smaller balls. This suggests that the collisions between 6.7 mm balls provided less mechanical energy for the reaction to occur than 9.5 mm balls, and that 12.5 mm balls led to fewer collision events than 9.5 mm balls. For this reason, 9.5 mm balls were used for the remainder of the study.

Next, the effect of milling time was investigated. Figure 2-1a shows the XRD patterns of as-milled powders with various milling times. With increasing milling time, the intensity of diffraction peaks associated with ZnO and HmIm (at  $\sim 18^\circ$  and  $\sim 21^\circ$  indicated with arrows) decreased relative to the peaks corresponding to ZIF-8. The result indicates that the reaction between ZnO and HmIm progressed steadily with milling time. However, there was an upper limit in milling time to produce crystalline ZIF-8. After 12 hours of milling, the sample was amorphous (Figure 2-1a). This is due to prolonged ball milling inducing excessive crystal defects [66,67]. By applying the

Scherrer equation onto the (011) diffraction peak (Figure S 2-3), the average crystallite size of the sample milled for 8 hours was estimated to be 46 nm.

The TGA results (Figure 2-1c) of the as-milled powders showed that a weight loss occurred between 120 and 200°C. The weight loss is related to the evaporation of unreacted Hmlm and can be used as an indicator of the progress in the reaction between Hmlm and ZnO; smaller weight loss up to 200°C indicates a smaller quantity of unreacted Hmlm remaining in the as-milled powder, thus more progress in the reaction during milling. As can be seen in Figure 2-1c, less weight loss is observed for the samples milled for longer durations. This further highlights that the reaction between ZnO and Hmlm progressed with milling time, consistent with the XRD data (Figure 2-1a). Importantly, the TGA result also shows that the specimens are thermally stable up to nearly 400°C, after which they start to decompose to ZnO.

The results of surface area analysis in Figure 2-1d shows that, longer milling times led to increased BET and Langmuir specific surface areas. Since the washed powder comprises ZIF-8 and unreacted ZnO, the increased specific surface areas indicate that prolonged milling time resulted in the production of a higher amount of ZIF-8. This trend is consistent with the results of the XRD and TGA studies reported above. The sample milled for 8 hours and washed with DI water exhibited BET and Langmuir specific surface areas of 1,367 and 1,503 m<sup>2</sup> g<sup>-1</sup>, respectively. These values are in reasonable agreement with the 69.3% conversion rate of ZnO estimated by TGA; at this conversion rate, the expected surface area is calculated as

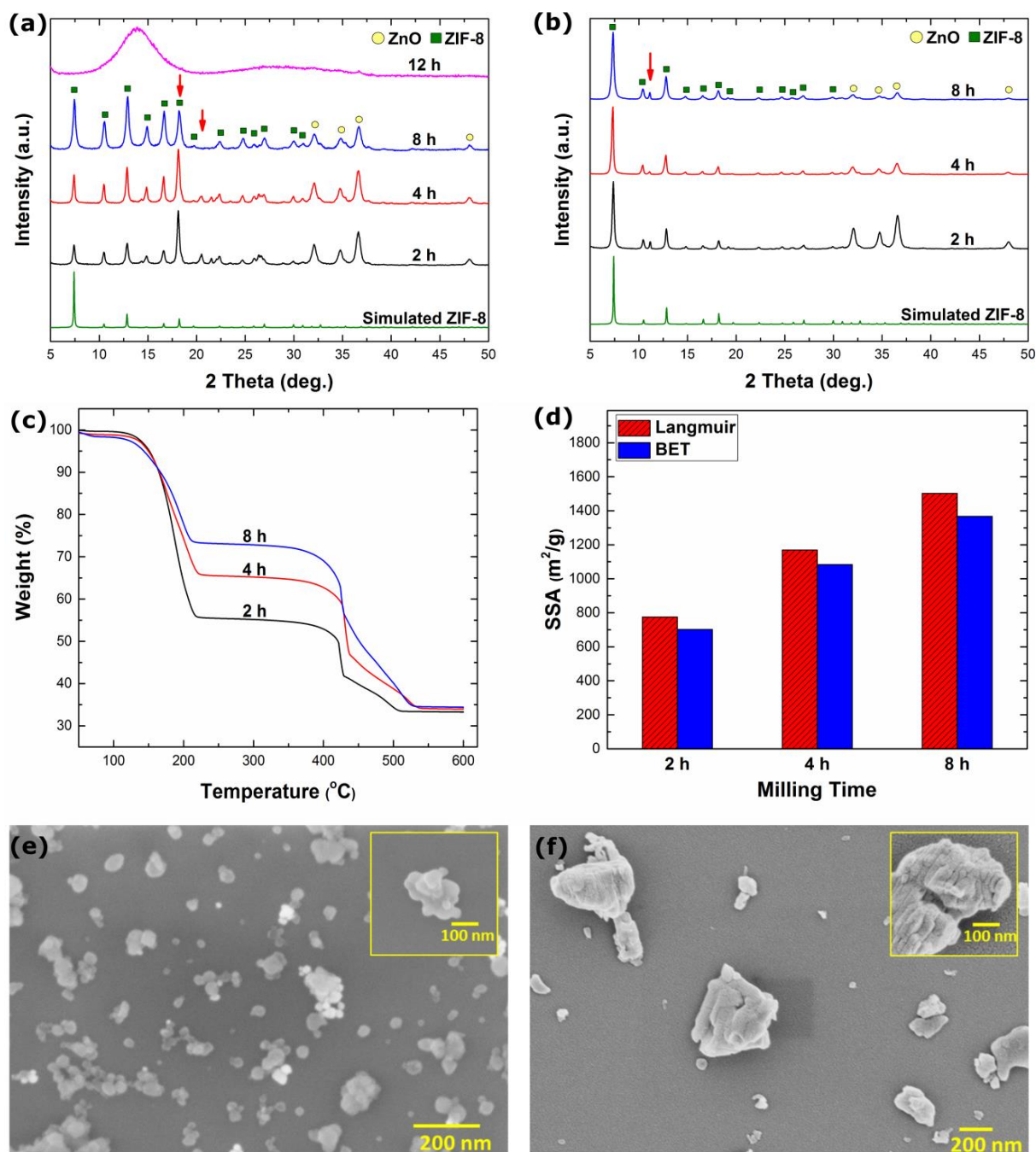
$$\text{Expected surface area} = \frac{69.3 \cdot 1947 + (100 - 69.3) \cdot 43.6}{100} = 1363 \text{ m}^2 \text{ g}^{-1} \quad (2-1),$$

where 1,947 m<sup>2</sup> g<sup>-1</sup> is the theoretical surface area of ZIF-8 and 43.6 m<sup>2</sup> g<sup>-1</sup> is the measured BET surface area of unreacted ZnO.



Figure 2-1e shows an SEM image of the sample milled for 8 hours and subsequently washed with DI water. It is evident that the particles are roughly spherical in shape and that their diameters are less than 100 nm (average particle size of  $37 \pm 17$  nm). There are some agglomerations as presented in the inset. Figure 2-1f shows the microstructure of the amorphous sample obtained after milling for 12 hours. The majority of amorphous particles are agglomerated and are larger than the crystalline nanoparticles obtained after milling for 8 hours, further supporting that ~8 hours is the optimal milling duration. This is due to the fact that prolonged milling resulted in partial welding of powders caused by local-heat and pressure generated during the collision events, leading to the formation of larger, amorphous particles.

Figure 2-1b shows the XRD patterns of the samples after removal of unreacted Hmlm via washing with DI water. It can be seen that the washing process did not alter the crystal structure. However, the relative intensity of a diffraction peak at  $\sim 7^\circ$  increased. In addition, an unidentifiable diffraction peak appeared at approximately  $11^\circ$  in the XRD patterns, as indicated with an arrow in Figure 2-1b. This extra peak has been reported in the literature [68–71] and proposed to be related to water molecules in the pore structure of ZIF-8. This proposal is supported by the fact that, when the samples were washed with ethanol instead of water, the extra diffraction peak was eliminated (Figure S 2-4). Ethanol-washing resulted in the BET and Langmuir specific surface areas of 1,412 and 1,543  $\text{m}^2 \text{g}^{-1}$ , respectively, which is similar to the values of water-washed samples, validating that the peak at  $11^\circ$  is due to entrapped water molecules instead of a structural difference.



**Figure 2-1** XRD patterns of a) as-milled and b) water-washed samples dry-milled for 2 to 12 hours using 9.5 mm balls in comparison with simulated ZIF-8 pattern, c) thermogravimetric analysis of as-milled samples in air, d) BET and Langmuir specific surface areas of water-washed samples, and SEM images of washed nanopowders milled for e) 8 hours and f) 12 hours

It is reported that ZnO can be converted to ZIF-8 by reacting with HmIm solutions for a prolonged period, resulting in the formation of a ZIF-8 layer on the surface of ZnO [72–74]. This may imply that, during the washing of as-milled powders, residual ZnO may react with

dissolved Hmlm in solvents. In order to study the extent of such events, an unmilled stoichiometric mixture of ZnO nanoparticles and Hmlm was subjected to the same washing process as for the as-milled samples, with water and ethanol. The XRD study of the washed sample revealed that the washed powder comprised only ZnO with no trace of ZIF-8 (Figure S 2-6). The result indicates that the time taken for the washing process is too short to cause the extent of the reaction detectable by XRD and thus validates the data in Figure 2-1.

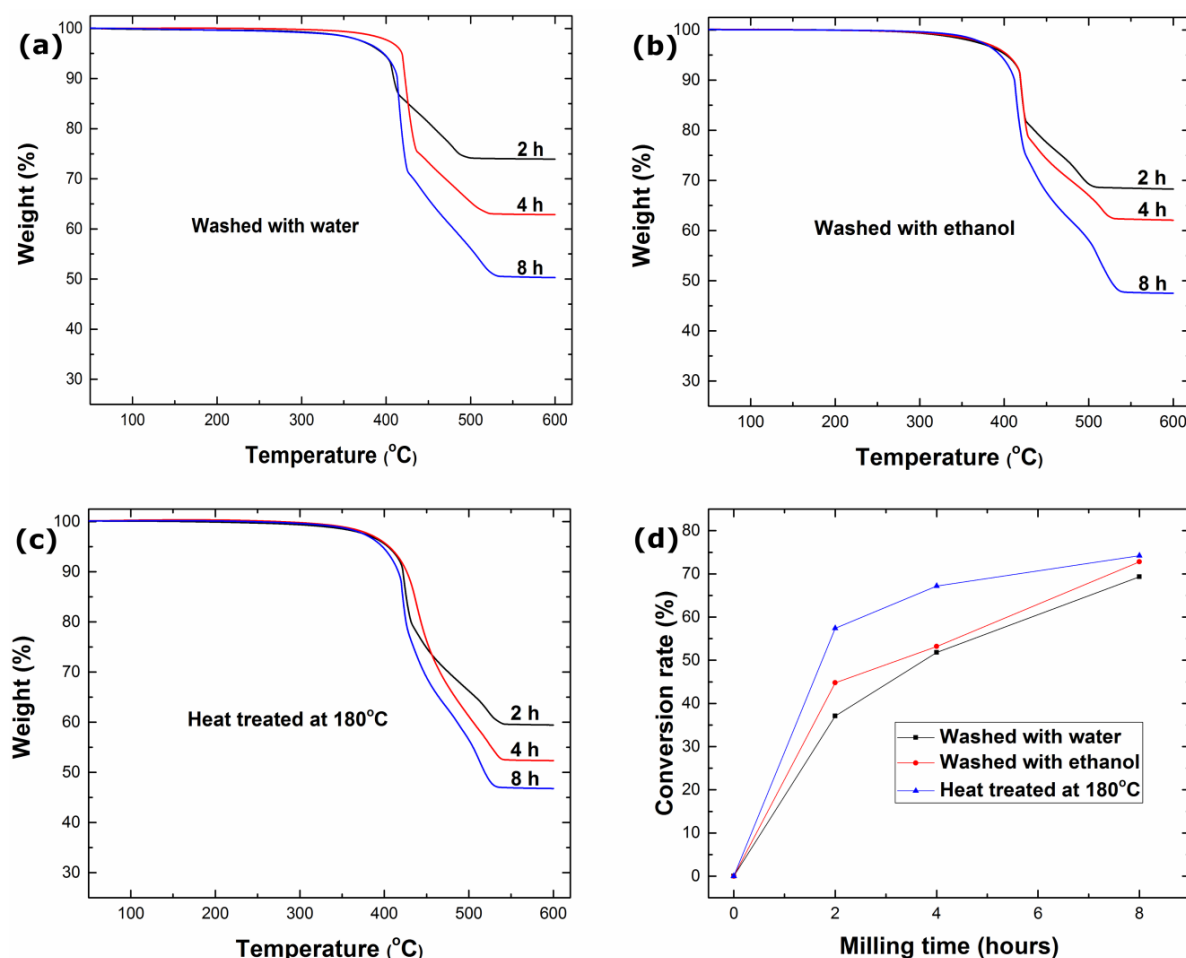
Alternative methods to remove un-reacted Hmlm from the samples were further explored. Since Hmlm can sublime at relatively mild temperatures below the thermal decomposition temperature of ZIF-8, the possibility of removing unreacted Hmlm by sublimation was studied. In order to determine the optimum sublimation temperature, the as-milled samples were heat-treated at 120, 150, and 180°C. As the temperature increased from 120 to 180°C, the XRD peak associated with Hmlm at  $\sim 18^\circ$  and  $\sim 21^\circ$  decreased (indicated with arrows in Figure S 2-5). Heat treatment at 180°C for 2 hours was required to completely remove unreacted Hmlm. The BET and Langmuir specific surface areas of the sample after heat treatment at 180°C for 2 hours were 1,450 and 1,592 m<sup>2</sup> g<sup>-1</sup>, respectively, again indicating that the novel sublimation protocol maintained nearly the same surfaces area as samples washed with water or ethanol to remove the unreacted Hmlm.

Although unreacted Hmlm can be removed either by washing or heat treatment, unreacted ZnO cannot be removed by using these methods. This fact can be exploited to estimate the ZnO-to-ZIF conversion rate, from the final weight-loss value in TGA measurements. Figure 2-2a-c show TGA curves of the samples after removing unreacted Hmlm by either washing or heat treatment at 180°C for 2 hours. No weight loss was observed below  $\sim 400^\circ\text{C}$  because the unreacted Hmlm had been removed via the post-milling treatment. The weight loss was completed at 480 – 530°C. The theoretical weight loss for the decomposition of ZIF-8 (227.6 g mol<sup>-1</sup>) into ZnO (81.4 g mol<sup>-1</sup>) is 64.3%. Since ZnO does not induce weight loss at this temperature range, when unreacted ZnO is present in the powder

after the removal of Hmlm, the weight loss should be reduced from 64.3%. Hence the ZnO-to-ZIF conversion rate can be calculated using the following formula:

$$\text{Conversion rate} = 100 \cdot \frac{\text{Weight loss (\%)}}{64.3 (\%)} \quad (2-2).$$

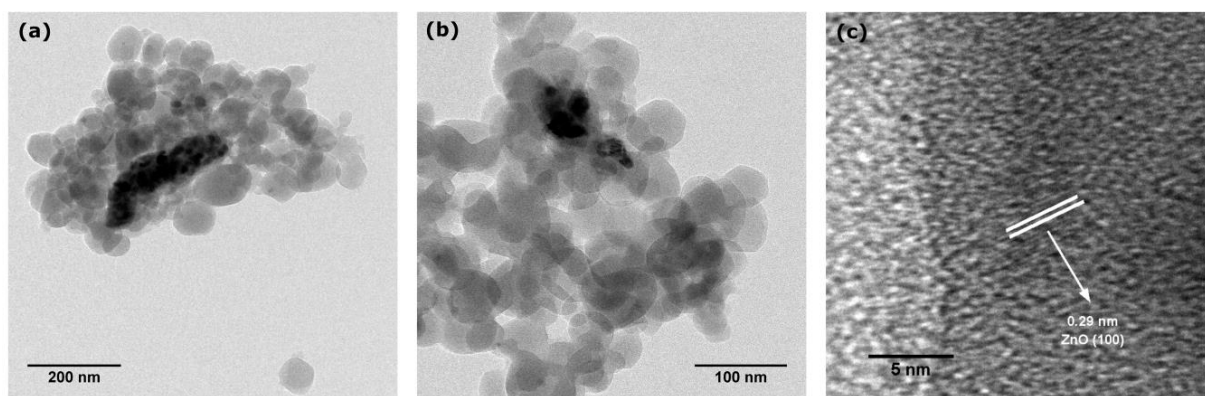
Figure 2-2d shows the ZnO-to-ZIF conversion rate as a function of milling time, for different methods to remove unreacted Hmlm. The conversion rate was higher for the heat-treated samples than for the washed samples. This difference indicated that further reaction occurred between unreacted ZnO and Hmlm during heat treatment. The difference was very small for the samples milled for 8 hours, suggesting that 8 hours of milling is nearly the endpoint beyond which no further reaction between the starting reactants occurs during milling.



**Figure 2-2** Thermogravimetric analysis of the dry-milled samples with different post-milling treatments to remove unreacted Hmlm; a) washed with water, b) washed with ethanol, and c) heat-treated at 180°; d) comparison of conversion rate as a function of milling time, for different post-milling treatments

It was also found that the use of a nonstoichiometric molar ratio of the starting materials with an excess amount of Hmlm ( $\text{ZnO}:\text{Hmlm} = 1:3$ ) did not improve the conversion rate of ZnO to ZIF-8 (Figure S 2-7).

TEM studies revealed that, after the removal of unreacted Hmlm, the powder milled for 8 hours consisted of ZIF-8 nanoparticles with primary particle sizes of 20 - 100 nm. Large aggregates of ZIF-8 often contained unreacted ZnO in their core (Figure 2-3a-c). The primary particle sizes are in good agreement with the average crystallite size of 46 nm determined by XRD.



**Figure 2-3** Transmission electron microscopy images of the sample dry-milled for 8 hours and subsequently heat treated at 180°C at different magnifications (a-c).

Based on the results, it is hypothesised that, the reaction between ZnO nanoparticles and Hmlm occurred during dry milling, as shown schematically in Figure 2-4: If ZnO nanoparticles have a small degree of agglomeration [64,75], nanoparticles can be fully transformed into ZIF-8 nanoparticles, because only a small diffusion length is required for reactant atoms to convert an entire ZnO particle into ZIF-8. Past studies indicate that, in order to fully convert ZnO into ZIF-8 in a green-chemistry approach, it is crucial to utilise ZnO nanopowders with particle size less than 20-30 nm [64,76]. For example, Tanaka *et al.* reported that only ~20 nm thick layer of ZIF-8 was formed on the surface of large ZnO particles after a prolonged reaction period. Considering the density of ZnO ( $5.61 \text{ g cm}^{-3}$ ) and ZIF-8 ( $0.95 \text{ g cm}^{-3}$ ), the conversion of ZnO into ZIF-8 induces volume expansion by a factor of 16.5. This volume expansion corresponds to the increase of layer thickness by a factor of 2.5. Hence, the study of Tanaka *et al.* shows that only the top ~10 nm thick layer of ZnO particle surface can be converted to ZIF-8 [64]. Stassen *et al.* [76] showed a similar result using chemical vapour deposition where complete transformation of a ZnO film to a MOF film occurred only for films with thickness less than 10 nm. The mechanochemically synthesised ZnO nanoparticles used in this chapter had an average particle size of 24.5 nm, which is small enough to enable the full conversion into ZIF-8.

If the ZnO nanoparticles are agglomerated, HmIm cannot reach the core of the ZnO agglomerates to react, as the ZIF-8 on the surface of ZnO agglomerates acts as a passivation layer. The TEM images show that dry milling cannot break the large agglomerates of ZnO nanoparticles even after 8 hours of milling. Hence, a small number of agglomerations present in the ZnO nanoparticles resulted in unreacted ZnO nanoparticles surrounded by ZIF-8 nanoparticles.

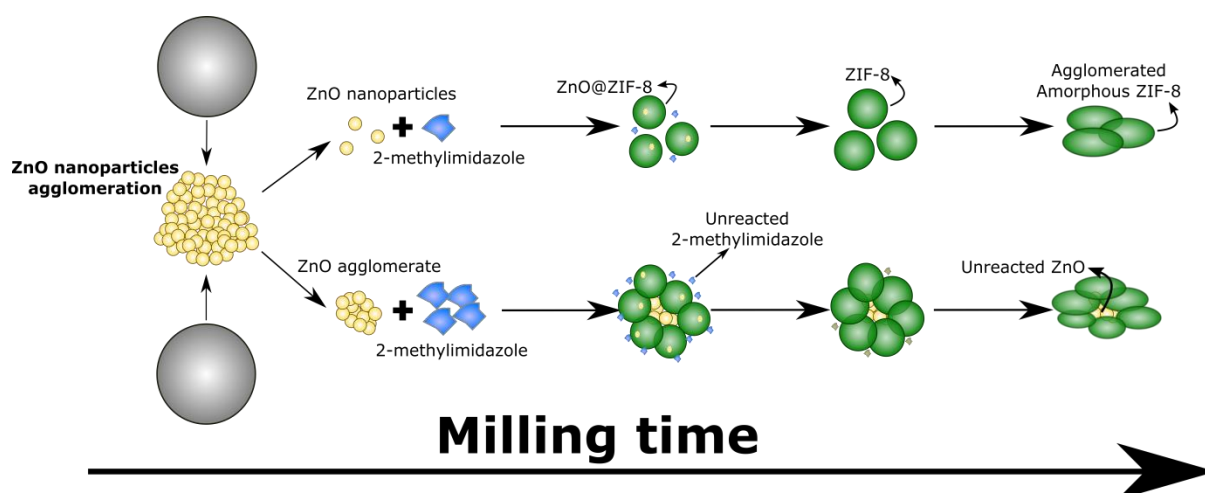


Figure 2-4 Schematic diagram of the reactions during ball milling of ZnO nanopowders and 2-methylimidazole stoichiometric mixture

### 2.5.2 Liquid assisted grinding

In order to overcome the agglomeration of ZnO nanopowders, liquid-assisted grinding (LAG) was investigated as an alternative to dry milling. In the 1.7 g of starting powder, 1.7 mL of methanol (ratio of 1  $\mu\text{L mg}^{-1}$ ) was added. The XRD results in Figure 2-5a shows that the conversion of ZnO to ZIF-8 occurred much faster in the presence of methanol than for dry milling; after 2 hours of milling and subsequent heat treatment, the majority of the ZnO nanopowders had transformed to ZIF-8 (Figure 2-5a).

After milling for 8 hours (the optimal condition for dry milling) and subsequent heat treatment at 180°C for 2 hours, no peak corresponding to ZnO was observed in the XRD pattern

(Figure 2-5b). The average crystallite size estimated from the broadening of (011) diffraction peak (Figure S 2-3) was 61 nm. TGA results showed that, after 2 hours of LAG and subsequent heat treatment at 180°C, 83.3% of ZnO nanopowders were converted to ZIF-8 nanopowders, corresponding to the weight loss of 53.6%. Increasing the milling time to 8 hours resulted in a weight loss of 65.7%, nearly the same as the theoretical weight loss of ZIF-8 alone, indicating the ZnO-to-ZIF conversion rate of approximately 100%. The BET and Langmuir specific surface areas of this sample (Figure 2-5d) were 1,751 and 1,885 m<sup>2</sup> g<sup>-1</sup>, respectively, which are among the highest experimental values reported in the literature and very close to the theoretical value of ZIF-8, 1,947 m<sup>2</sup> g<sup>-1</sup> [9]. SEM and TEM studies (Figure 2-5e-f) revealed that the sample comprised poorly faceted particles of 30 – 100 nm in diameter (average particle size of 81 ± 31 nm; Figure S 2-11c), which is in good agreement with the DLS study (Figure S 2-8d) and the average crystallite size of 61 nm calculated from the X-ray diffraction pattern. Although there was no evidence of contamination in XRD patterns and SEM studies of the milled samples, inductively coupled plasma - optical emission spectrometry (ICP-OES) analysis was employed to trace the level of iron contaminations (Figure S 2-9) originated from the milling balls and milling container. The results showed that the concentration of iron was less than 0.1 wt% which is consistent with the previous report [65].

More importantly, there was a complete absence of a ZnO-core, in contrast to the ZIF-8 particles formed via dry milling. Therefore, it is clear that the addition of a small amount of methanol in the starting powder not only enhanced the rate of mechanochemical reaction [77], but also resulted in greater dispersion and de-agglomeration of ZnO nanopowders. The latter function of LAG, which has not been reported previously, is vital for enabling the full conversion of ZnO into ZIF-8, because the ligand cannot reach the core of ZnO agglomerates to fully convert them into ZIF-8.



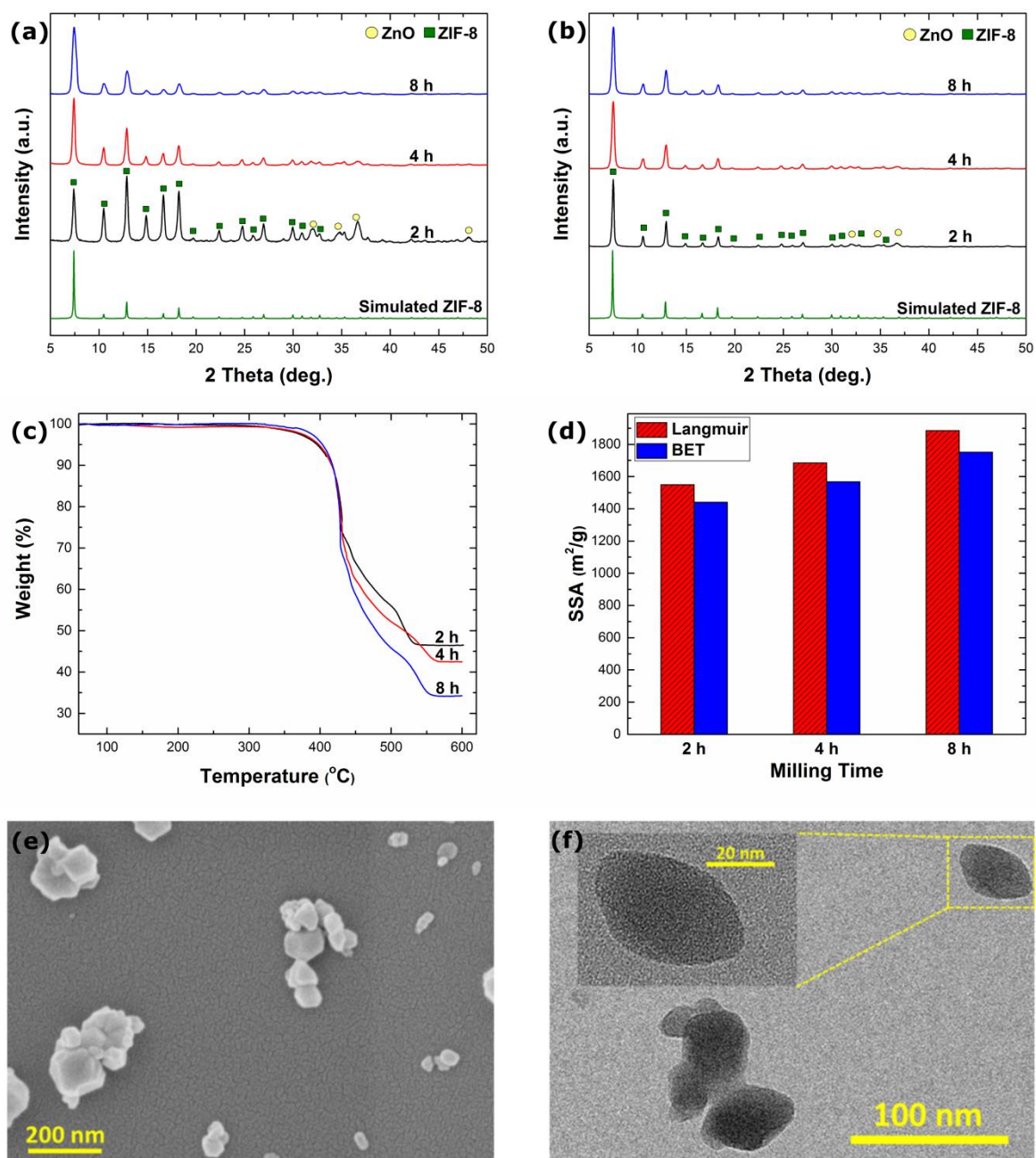


Figure 2-5 XRD patterns of a) as-milled and b) heat-treated samples, prepared using a liquid-assisted grinding method in comparison with simulated ZIF-8 pattern; c) thermogravimetric curves and d) BET and Langmuir specific surface areas of heat-treated samples; e) scanning and f) transmission electron microscopy images of the sample milled for 8 hours in the presence of methanol and subsequently heat-treated at 180°C

In summary, the LAG method demonstrated the capability of producing *nano-scale* ZIF-8 powders with a *low degree of agglomeration* by using a *stoichiometric reaction* without the

need for an extra amount of the ligand. *ZnO raw material* was utilised as an inexpensive reagent which does *not require the use of hazardous solvents* and results in water as the by-product after reaction with HmIm. This one-step process enabled the *full conversion of ZnO*, thus no wastage of the raw material. Although each of these features was separately achieved using different methods in the past, this is the first time all these features were concurrently achieved using a single synthesis method (Table 2-1).

### 2.5.3 Dye adsorption

As shown in Figure 2-5e and f, the resulting particles were irregularly shaped and poorly faceted. This is because, during the mechanochemical conversion of ZnO to ZIF-8, solid ZnO nanoparticles act as a template for ZIF-8 particles where atomic diffusion of zinc ions within the solid particle governs the reaction. In contrast, solvent-based precipitation techniques often result in ZIF-8 particles with well-developed facets, due to the fact that zinc ions and 2-methylimidazoles can freely move in the solvent to build ZIF-8 crystals on seed particles almost epitaxially.

In order to study the surface chemistry and organic-pollutant adsorption behaviour of the mechanochemically synthesised ZIF-8 nanopowders, the absorption of two commonly-used model contaminants, i.e. RhB and MB, were characterised and the results were compared with geometrically-shaped ZIF-8 nanopowders synthesised using a conventional method, i.e. a solvent-based precipitation technique. The ZIF-8 nanopowders synthesised using a methanol-based technique had rhombic dodecahedral shapes (Figure S 2-10c), an average particle size of  $134 \pm 21$  nm (Figure S 2-11), and BET and Langmuir surface areas of 1,698 and  $1,834 \text{ m}^2 \text{ g}^{-1}$ , respectively (Figure S 2-10b). It is worth mentioning that in the methanol-based method, an extra amount of the ligand was required, and it still resulted in a very low yield (~10% based on the zinc precursor).

Figure 2-6a shows that mechanochemically synthesised nanopowders are more effective in the adsorption of RhB and MB. The raw UV-Vis absorbance spectra of the specimen are presented in Figure S 2-12. After 30 minutes of exposure in the dark, 29.1% of MB and 93.9% of RhB were removed by the mechanochemically synthesised nanopowders. On the other hand, in the presence of conventionally synthesised nanopowders, the amount of dye adsorption was reduced to 3.3% of MB and 41.6% of RhB.

The size of RhB and MB molecules are larger than the pore sizes of ZIF-8 and hence they are adsorbed onto the external surface of ZIF-8, not onto the internal pores [52,72,78]. The external surface area of the ZIF-8 particles can be estimated from their average particle size by assuming that the nanoparticles are quasi-spherical. Considering the average particle size of 81 and 134 nm for mechanochemically and conventionally synthesised ZIF-8 nanopowders, the external surface areas of these samples were estimated to be 75.6 and 45.7 m<sup>2</sup> g<sup>-1</sup>, respectively, using the following equation (see Supplementary Information) [79]:

$$S_{ext.} = \frac{6000}{\rho * D} \quad (2-3),$$

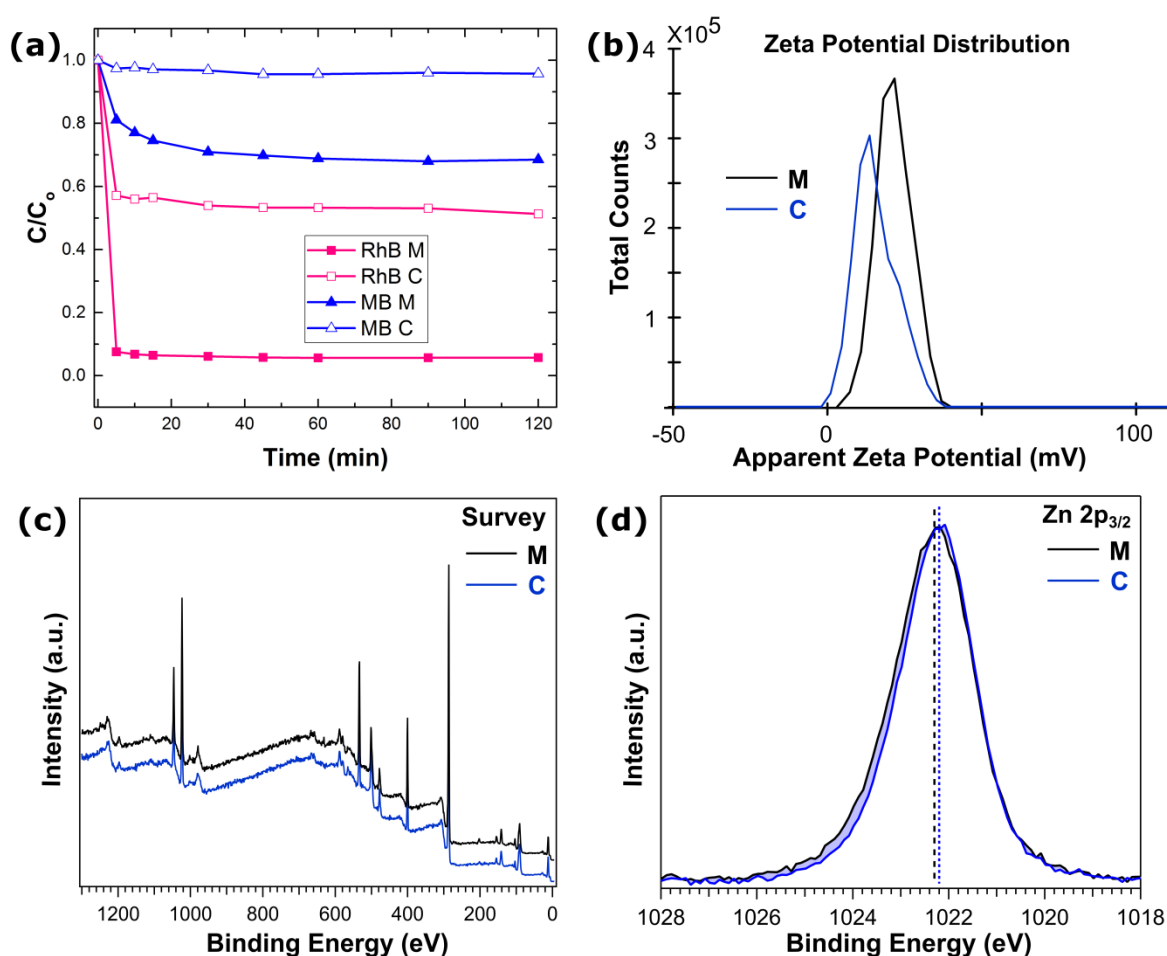
where  $S_{ext.}$  is the external surface area (m<sup>2</sup> g<sup>-1</sup>),  $\rho$  is the density of ZIF-8 (0.98 g cm<sup>-3</sup>), and  $D$  is the average particle diameter (nm). Because of the size difference, the external specific surface area of mechanochemically synthesised ZIF-8 was 1.65 times higher than the conventionally synthesised ZIF-8. However, the difference in dye-adsorption capacity was more than the difference in external surface area. The dye adsorption capacity of mechanochemically synthesised ZIF-8 was higher than that of the conventionally synthesised ZIF-8, by more than 8 times for RhB and 2 times for MB. Therefore, the increased surface area (i.e. smaller particle size) alone cannot be accounted for the improved dye-adsorption of mechanochemically synthesised ZIF-8. The difference in the dye-adsorption capacity between the two ZIF-8 nanopowders should be attributed not only to

the difference in their particle size and external surface areas but also to the difference in their surface chemistry.

It is reported that, depending on synthesis conditions, different functional groups, such as hydroxyls and low coordinated Zn atoms along with methylimidazole groups, coexist on the external surface of ZIF powders [43,44,51,80]. Thus, synthesis methods influence the surface chemistry of resulting ZIF-8 particles. Figure 2-6b shows zeta potential distributions of the two ZIF-8 samples in water (pH 8.9). It can be seen that the mechanochemically synthesised sample possesses a more positive surface charge ( $20.9 \pm 0.5$  mV) than its counterpart ( $13.3 \pm 1.1$  mV). The difference in zeta potential was attributable to the shape difference between the two ZIF-8 samples. In the geometrically-shaped samples, crystal facets were exposed to the external surface of the particles where atoms are regularly ordered. In contrast, the randomly-shaped samples would have more surface defects such as Zn atoms with low coordination numbers, which create a stronger positive charge on the surface [51]. It has been reported that cationic organic dyes can be strongly adsorbed on the positively-charged external surface of ZIF-8, via the interaction between the low-coordinated Zn and dye's unpaired electrons (such as O in RhB and N in MB) [51,78]. Thus, the zeta potential distribution suggests that mechanochemically synthesised particles have high organic dye uptakes because of a high number of low coordinated Zn atoms on the surface.

To further examine the impact of the mechanochemical synthesis on the surface chemistry of ZIF-8 samples, X-ray photoelectron spectroscopy (XPS) measurements, a surface-sensitive technique, were carried out (Figure 2-6c, Figure 2-6d, and Figure S 2-13). As inferred from the XPS survey spectra (Figure 2-6c), the overall elemental compositions of the mechanochemically and conventionally synthesised ZIF-8 nanopowders were very similar. Nevertheless, peak fitting of the high-resolution Zn 2p core-level spectra revealed a peak shift by 0.1 eV towards higher binding energies, as well as a broadening of the lineshape by  $> 0.1$  eV (Figure 2-6d), for the milled samples. The former is caused by a re-

arrangement of the electronic cloud of the surface atoms, which can be ascribed to bond cleavage or undercoordination induced by the mechanochemical process [81]. The peak broadening confirms a higher degree of disorder, i.e. a lower degree of crystallinity, on the surface of milled samples: the different configurations in which the atoms rearrange yield a large number of final-state configurations for the photoemitted electrons, therefore a broadened lineshape [81]. The details of the peak fitting are presented in Table 2-2.



**Figure 2-6** (a) Variation of relative concentration of MB and RhB in water in the presence of mechanochemically (M) and conventionally (C) synthesised ZIF-8 nanopowders as a function of time under a dark condition; (b) zeta potential distribution of the mechanochemically (M) and conventionally (C) synthesised ZIF-8 nanopowders at pH 8.9; (c) Survey XPS spectra and (d) high-resolution Zn  $2p_{3/2}$  XPS spectra of the mechanochemically (M) and conventionally (C) synthesised ZIF-8 nanopowders

The superior dye-uptake capability of mechanochemically processed MOF nanopowders makes them an excellent material for applications in waste treatment, wherein dual adsorptions of small and large contaminants can be realised at the same time. Their high internal specific surface area allows the efficient adsorption of small atomic-scale contaminants such as heavy metal ions, while an active external surface with a high degree of particle dispersion enables the adsorption of larger contaminants such as organic molecules.

For these applications, it is necessary to separate and recover the nanoparticles from water after contaminant adsorption, which is difficult to achieve using dispersed nanoparticles. It is expected that well-dispersed ZIF-8 nanoparticles can be used in water-remediation applications by adopting the techniques developed for other nanoparticles [82]. For example, efficient separation and recovery of free-standing nanoparticles from water have been demonstrated by means of magnetic separation [83]. Zheng *et al.* demonstrated the synthesis of magnetic  $\text{Fe}_3\text{O}_4@\text{ZIF-8}$  nanocomposites in the application to remove  $\text{UO}_2^{2+}$  [49] and methylene blue [46] from water. Immobilisation of nanoparticles on the surface of a macroscopic object is another approach to provide nanoparticles with bulk handling capability while preventing particle agglomeration to retain their high surface areas [84–87].

## 2.6 Conclusions

This study demonstrated that well-dispersed ZIF-8 nanopowders can be produced in a green and scalable way and that the resulting nanoparticles have unique characteristics suitable for water remediation applications. A mechanochemical approach was adopted to produce ZIF-8 to achieve all of the following features at the same time: (1) the use of ZnO raw material thus inexpensive and no need for using hazardous solvents, (2) the use of a stoichiometric reaction without the need for extra ligand thus no wastage of the raw material, (3) full conversion of ZnO thus no wastage of the raw material, (4) scalability, (5) one-step

process with simple-to-control operation parameters, (6) no by-product generation except water, (7) nano-scale of the resulting powder, and (8) a low degree of agglomeration in the resulting powder. Although each of these features was separately reported in the past, no other technique is capable of simultaneously achieving all these features. In this study, the details of the critical processing conditions including milling-ball size, milling time, and post milling treatment that influence the conversion yield were analysed. Importantly, it was found that the use of a small amount of methanol in LAG is critical to breaking the agglomeration of ZnO nanoparticles and, in turn, to the subsequent full conversion of ZnO into ZIF-8 nanoparticles. This function of LAG was not recognised previously.

Liquid-assisted grinding for 8 hours and subsequent heat treatment at 180°C resulted in ZIF-8 nanoparticles of ca 80 nm in diameter, with a conversion yield of almost 100%, in a gram scale. Due to the high crystallinity and low degree of agglomeration, the particles had a specific surface area of 1,885 m<sup>2</sup> g<sup>-1</sup>, close to that of the theoretical maximum of 1,947 m<sup>2</sup> g<sup>-1</sup> and among the highest reported for ZIF-8. Mechanochemically synthesised ZIF-8 nanoparticles had more adsorption sites for model organic pollutants than ZIF-8 made from a conventional methanol-based precipitation method, due not only to the high surface-to-volume ratio of nanoparticles, but also to the higher number of surface defect sites associated with their irregular shapes. This renders mechanochemically synthesised ZIF-8 an excellent material for the removal of both small (i.e. heavy metal ions) and large (i.e. organic molecules) contaminants at the same time.

The study has provided a detailed understanding of the limitations and advantages of mechanochemical synthesis of ZIF-8 from ZnO, one of the simplest and most inexpensive metal precursors. Since ZnO nanoparticles of sizes less than 30 nm are readily available as commercial products, the new approach demonstrated in this study may be applicable to the large-scale production of ZIF-8 nanoparticles. The generalizable methodology can be also

applied to other insoluble metal oxides/hydroxides [53] or ligands [63] to synthesise MOF nanoparticles with unique surface chemistry for environmental applications.

## 2.7 References

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## 2.8 Supplementary Information

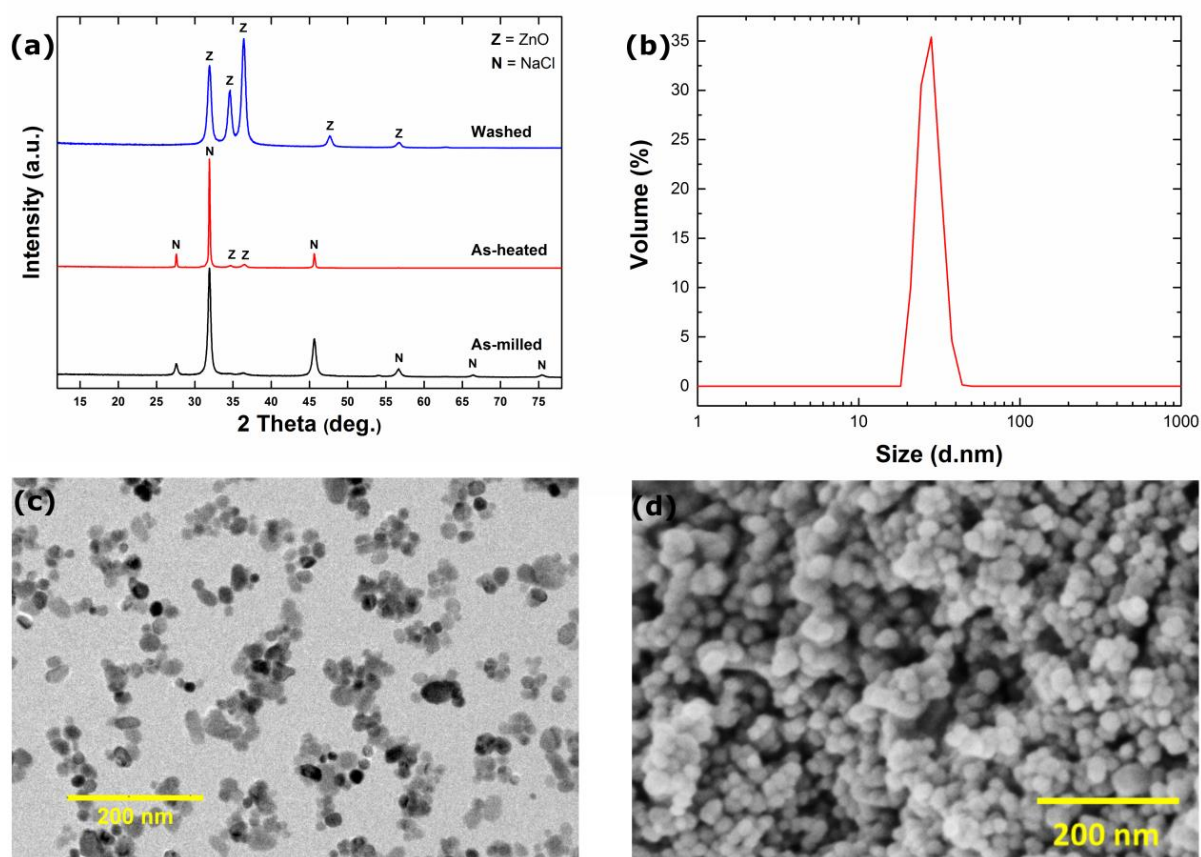


Figure S 2-1 a) XRD patterns of mechanochemically synthesised ZnO nanopowders, as-milled, as-heated at 400°C and after washing; b) DLS particle size distribution, c) transmission and d) scanning electron microscopy images of the ZnO nanopowders

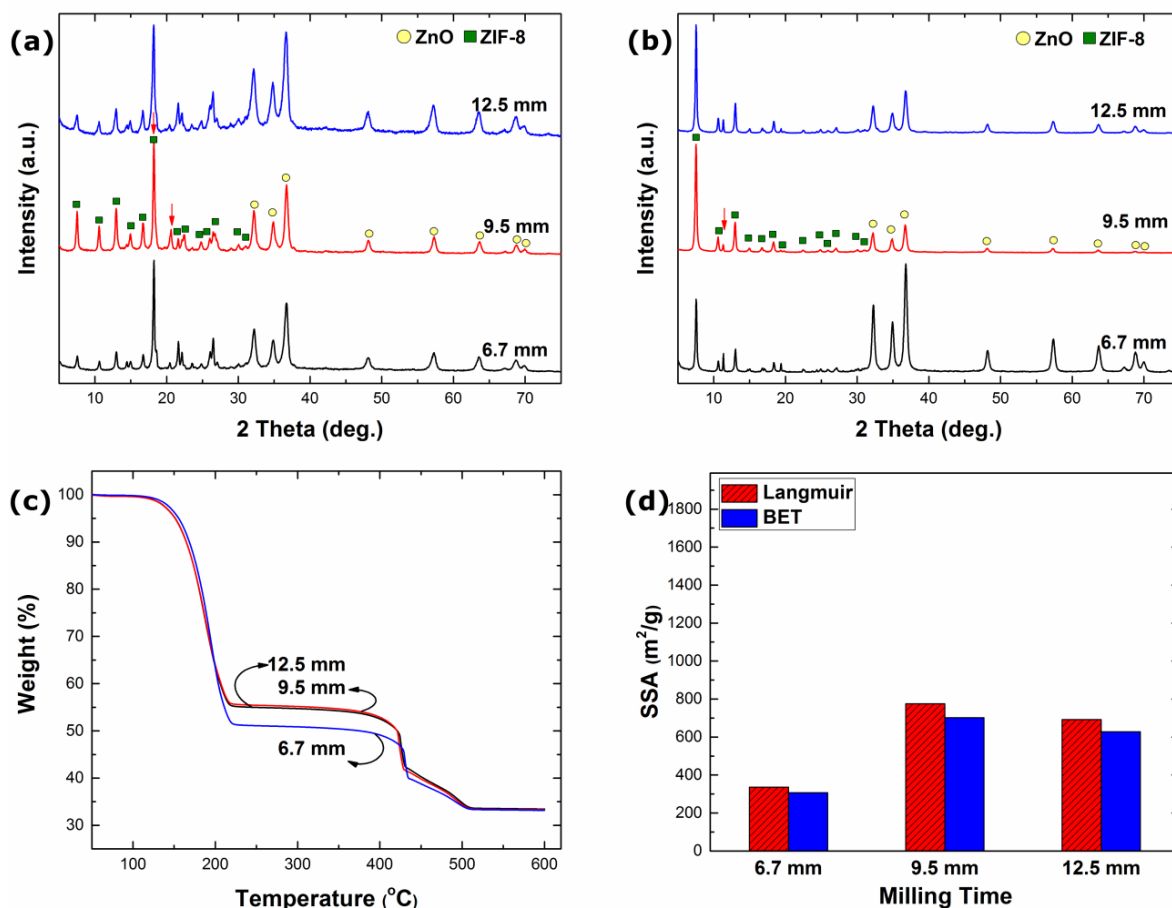


Figure S 2-2 XRD patterns of a) as-milled, and b) water-washed samples dry-milled with different sizes of milling balls for 2 hours; c) thermogravimetric curves of as-milled samples; d) BET and Langmuir specific surface areas of water-washed samples

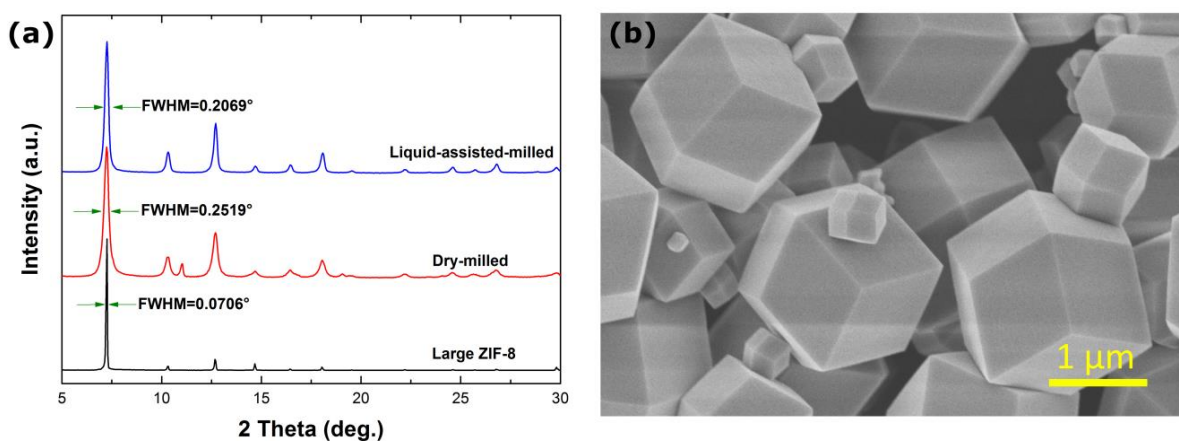


Figure S 2-3 (a) XRD patterns of dry-milled and liquid-assisted-milled ZIF-8 nanoparticles in comparison with large ZIF-8 particles, showing the peak broadening of the milled samples; (b) SEM image of the large ZIF-8 particles synthesised via a water-based precipitation method

**Note:** Large ZIF-8 particles were synthesised by mixing aqueous solutions of zinc acetate and 2-methylimidazole with a ratio of 1:16 and stirring for 24 hours at room temperature. The powders were collected and washed three times with DI water.

The particles were intentionally made into large sizes, solely for the purpose of measuring the instrumental peak broadening in the XRD analysis and were not used in the study of dye-adsorption performance.

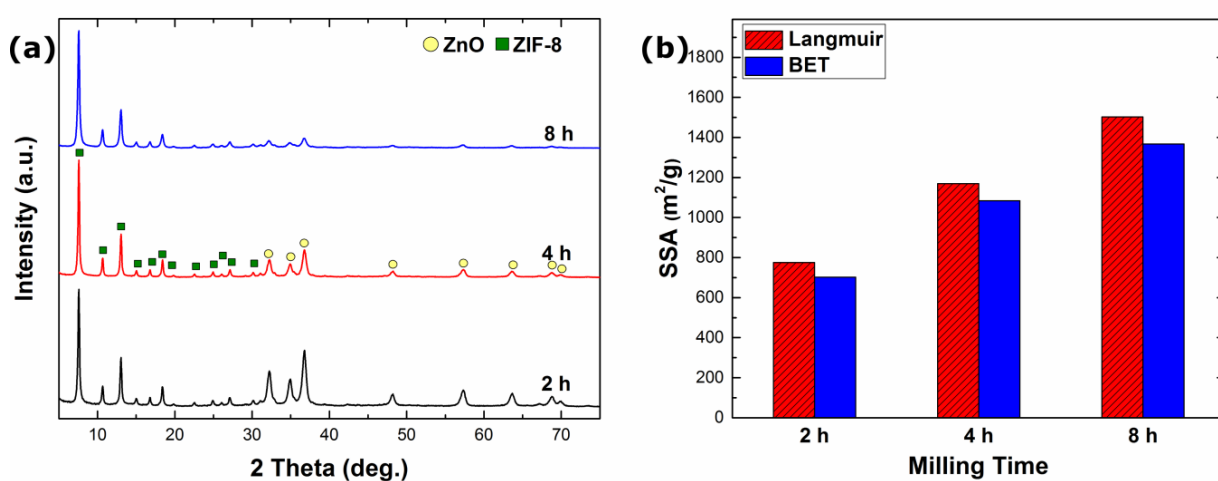


Figure S 2-4 a) XRD patterns and b) BET and Langmuir specific surface areas of samples dry-milled for different times and subsequently washed with ethanol



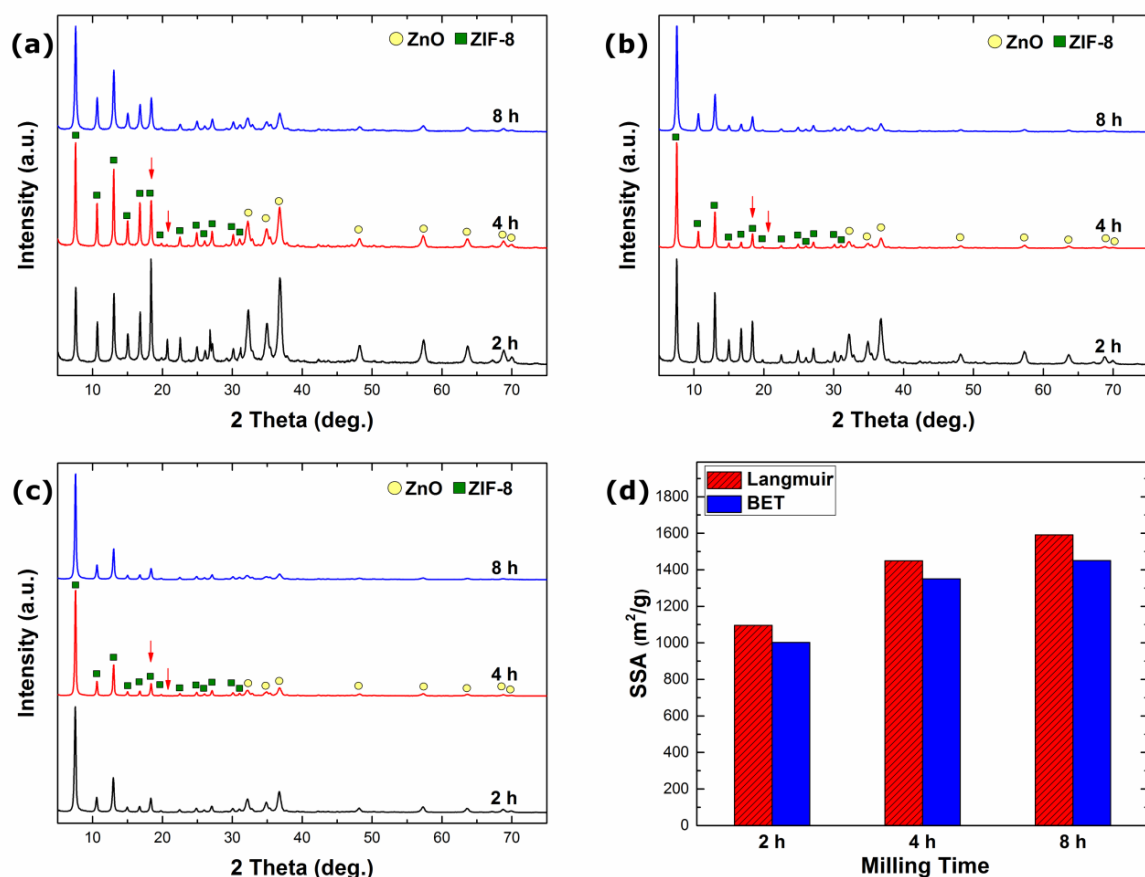


Figure S 2-5 XRD patterns of samples dry-milled for different times and subsequently heated at a) 120, b) 150, and c) 180°C for 2 hours in air; d) BET and Langmuir specific surface areas of samples heat-treated at 180°C for 2 hours

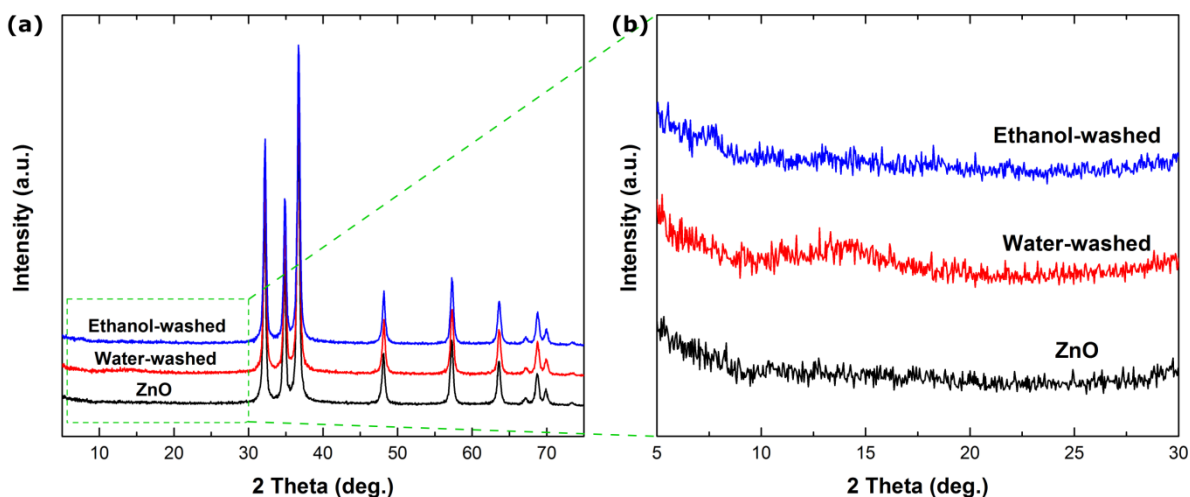


Figure S 2-6 (a) XRD patterns of the un-milled ZnO nanopowders mixed with a stoichiometric amount of Hmlm (not milled) and subjected to the same washing process with water/ethanol as for milled samples ; (b) enlarged XRD patterns in the 2 theta range of 5-30°

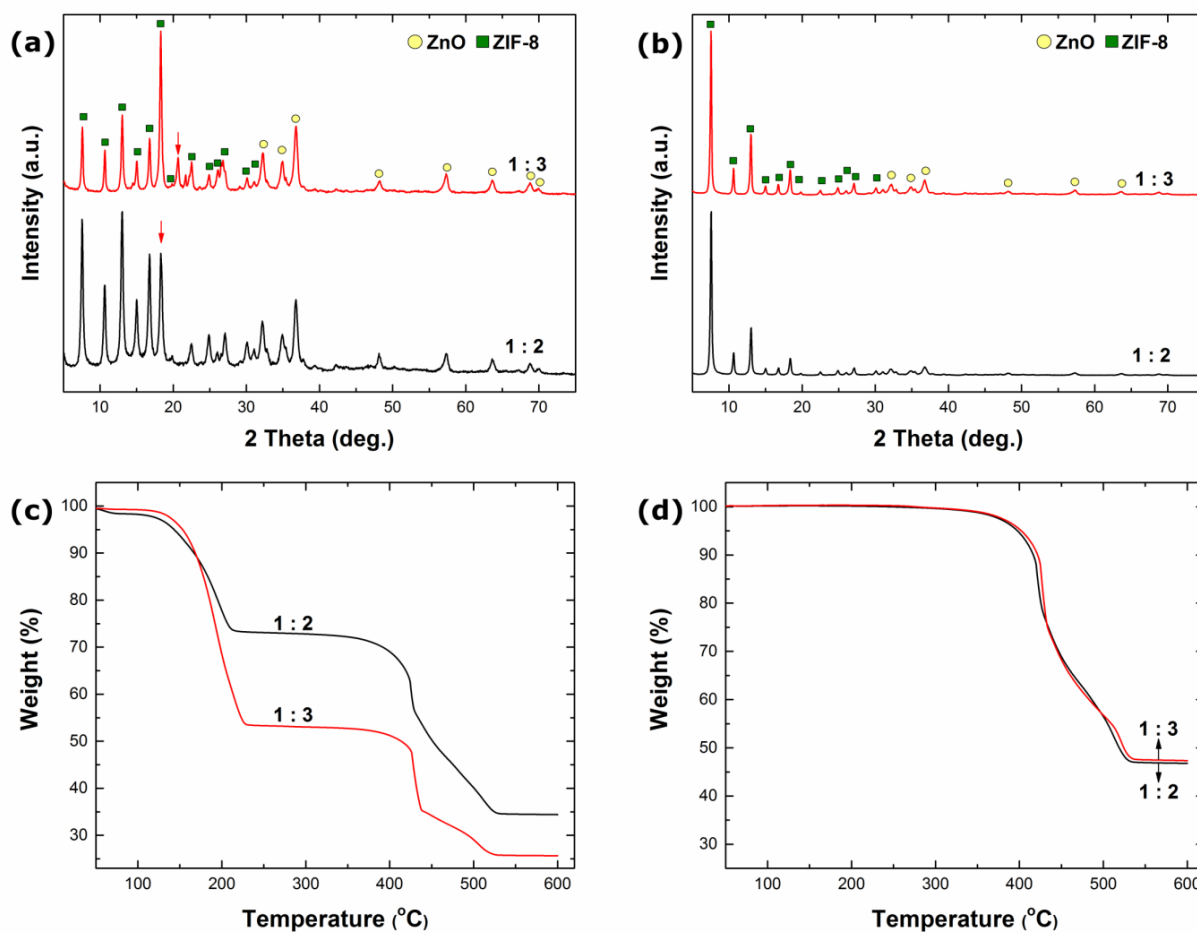
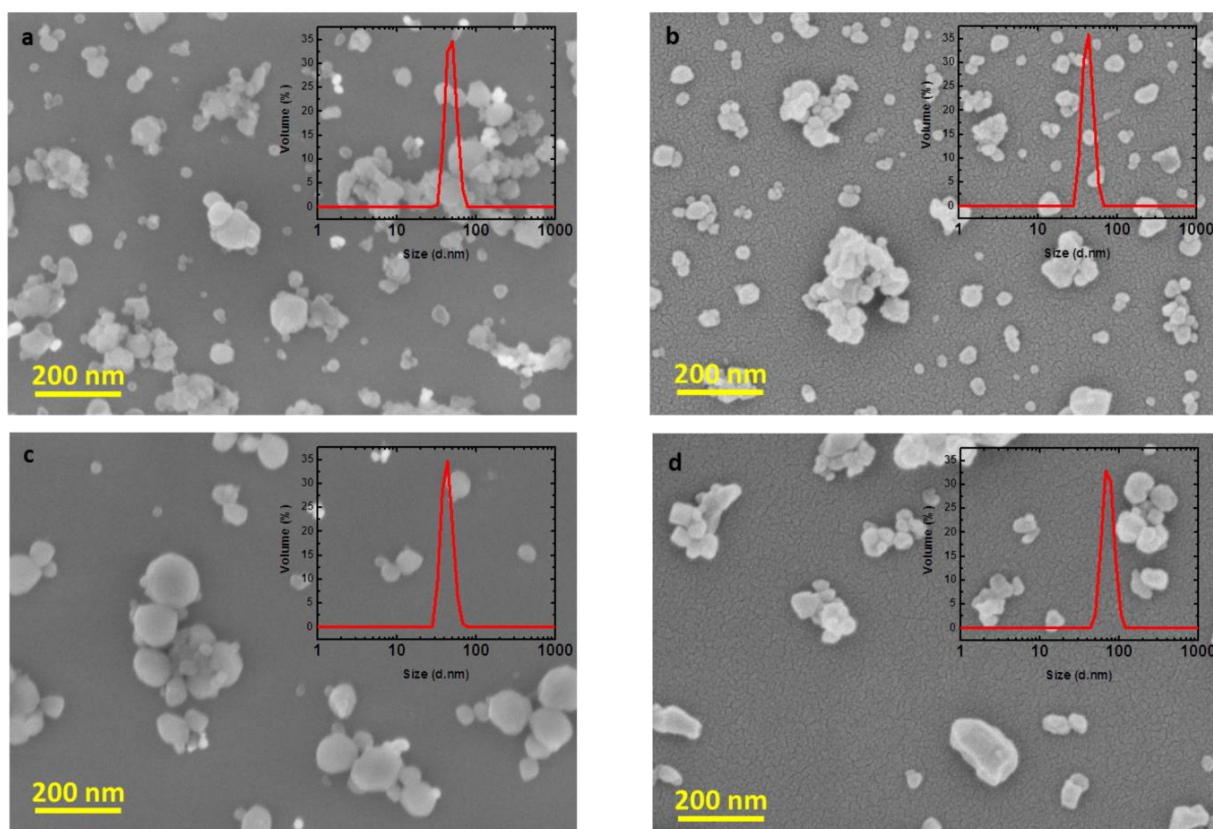
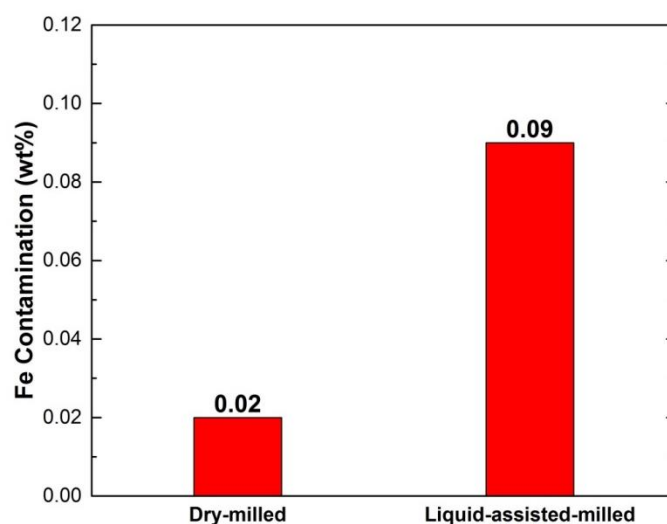


Figure S 2-7 XRD patterns and thermogravimetric curves of the a,c) as-milled and b,d) heat-treated samples that were dry-milled for 8 hours, comparing the samples with an excess amount of methylimidazole (ZnO:methylimidazole = 1:3) and its counterpart having the stoichiometric ratio of reagents (ZnO:methylimidazole = 1:2)



**Figure S 2-8** Scanning electron microscopy images of samples dry-milled for 8 hours and subsequently a) water-washed, b) ethanol-washed, c) heat-treated at 180°C, and d) liquid-assisted milled and subsequently heat-treated at 180°C. Inset: particle size distribution of the corresponding samples



**Figure S 2-9** Inductively coupled plasma - optical emission spectrometry (ICP-OES) analysis of the dry-milled and liquid-assisted-milled ZIF-8 nanoparticles, showing the level of Fe contamination after milling for 8 hours

**Note:** Samples were dissolved in 10% nitric acid and diluted to proper concentrations. The inductively coupled plasma - optical emission spectrometry (ICP-OES) analysis was carried out using 5110 ICP-OES (Agilent, USA), and a multi-element standard external calibration curve was utilised to measure the concentrations of zinc and iron.

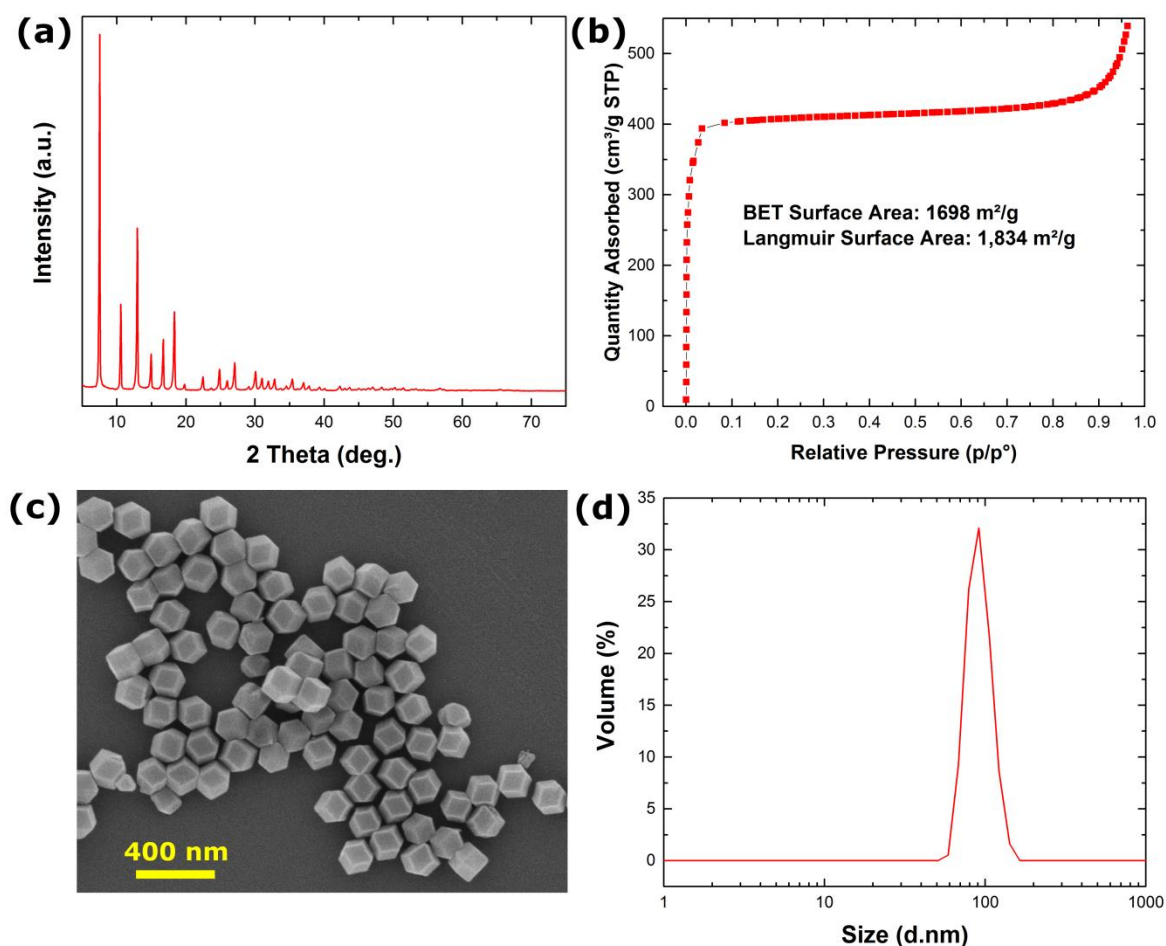
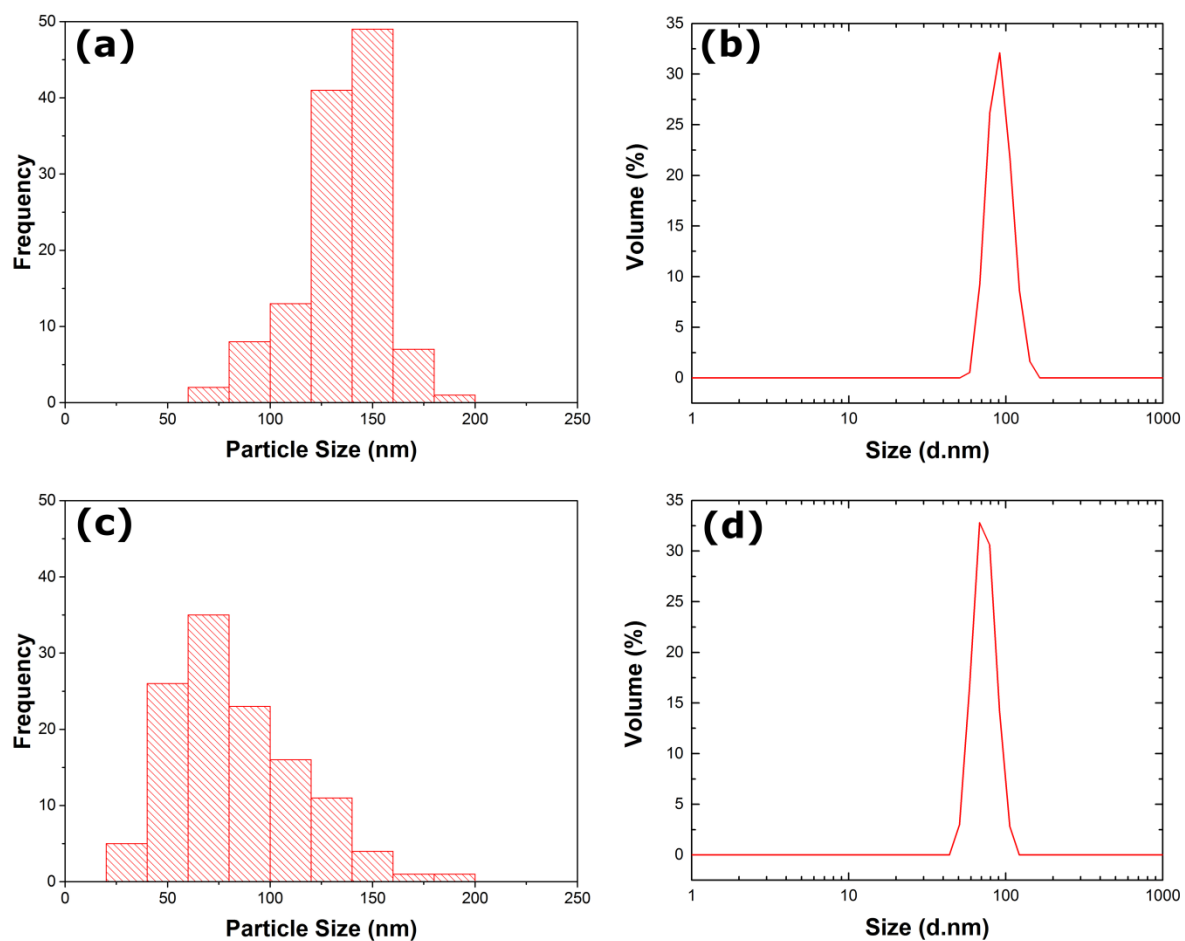


Figure S 2-10 (a) XRD pattern; (b) nitrogen adsorption isotherm; (c) SEM image; and (d) DLS size distribution of the ZIF-8 nanopowders synthesised via a methanol-based method



**Figure S 2-11 Histogram of particle sizes obtained from SEM micrographs of the a) conventionally and c) mechanochemically synthesised ZIF-8 nanopowders (more than 100 particles were measured.); DLS size distributions of b) conventionally and d) mechanochemically synthesised ZIF-8 nanopowders**

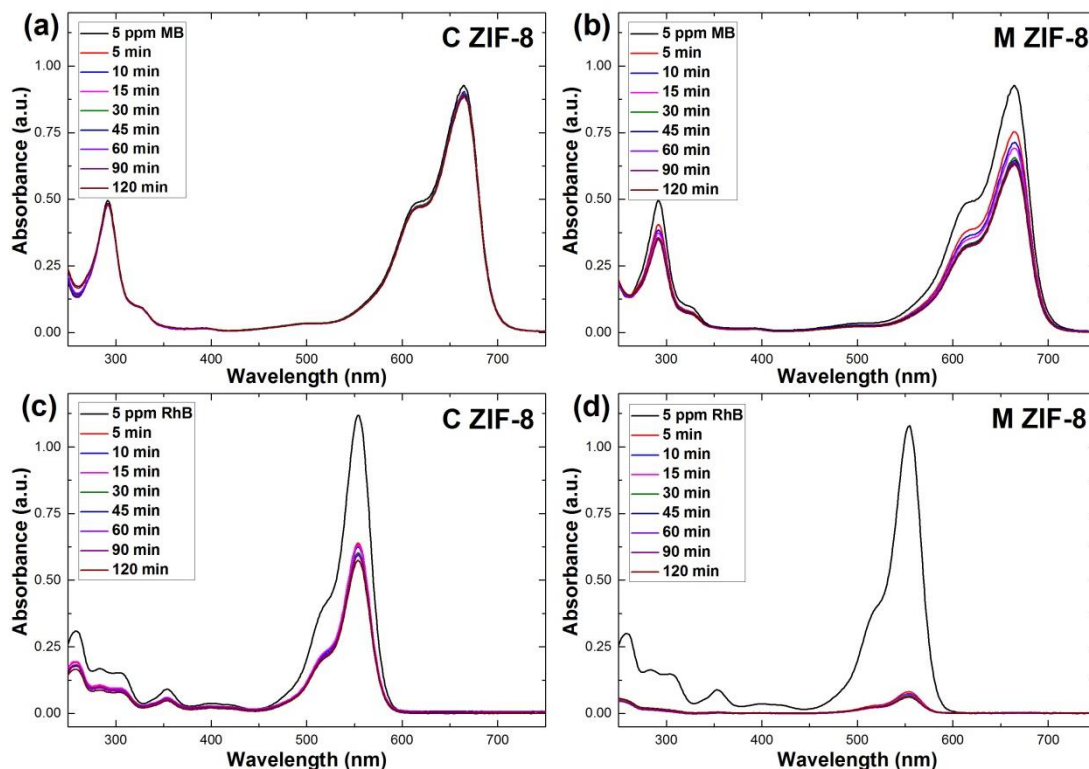


Figure S 2-12 UV-Vis absorbance spectra of 5 ppm methylene blue (MB) in the presence of 25 mg of (a) conventionally and (b) mechanochemically synthesised ZIF-8 nanopowders; UV-Vis absorbance spectra of 5 ppm Rhodamine B (RhB) in the presence of 25 mg of (c) conventionally and (d) mechanochemically synthesised ZIF-8 nanopowders

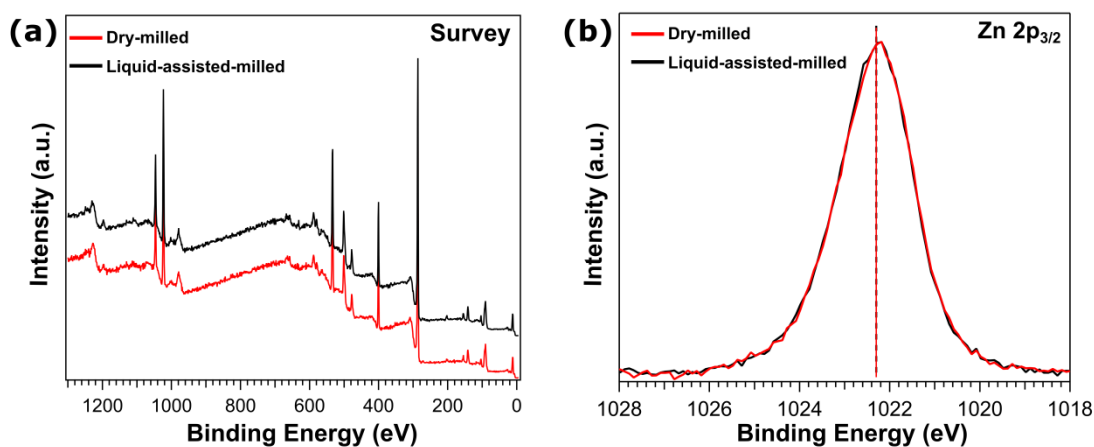


Figure S 2-13 (a) Survey XPS spectra and (b) high-resolution Zn 2p<sub>3/2</sub> XPS spectra of the dry-milled and liquid-assisted-milled ZIF-8 nanoparticles

Table 2-1 Key features of the green/solvent-free synthesis of ZIF-8

| Synthesis Method                           | Reagents                                              | Ratio of the reagents                  | Solvent(s)/Medium             | Product properties                                       | By-product                | Reference        |
|--------------------------------------------|-------------------------------------------------------|----------------------------------------|-------------------------------|----------------------------------------------------------|---------------------------|------------------|
| Supercritical CO <sub>2</sub> (pre-milled) | ZnO and HmIm powders                                  | Minimum 10 mol% excess ligand          | supercritical CO <sub>2</sub> | Pure sub-micron ZIF-8 particles (highly agglomerated)    | Water                     | [1]              |
| Extrusion                                  | Basic zinc carbonate and HmIm powders                 | Large quantity of excess ligand        | Solvent-free                  | Pure ZIF-8 particles (microstructure is not reported)    | Water and CO <sub>2</sub> | [2]              |
| Melting ligand                             | ZnO film and HmIm powder                              | Large quantity of excess ligand        | Solvent-free                  | Supported ZIF-8 films                                    | Water                     | [3]              |
| High pressure (hydraulic press)            | ZnO and HmIm powders                                  | Stoichiometric ratio                   | Solvent-free                  | Not fully converted                                      | Water                     | [4]              |
| Mechanochemistry                           | ZnO and HmIm powders                                  | Stoichiometric ratio                   | Liquid-assisted-grinding      | Not fully converted (microstructure is not reported)     | Water                     | [5,6]            |
| Mechanochemistry                           | ZnO and HmIm powders                                  | Stoichiometric ratio                   | Solvent-free                  | Not fully converted                                      | Water                     | [7]              |
| Mechanochemistry                           | ZnO + 10 mol% zinc acetate dihydrate and HmIm powders | Stoichiometric ratio with 10% additive | Solvent-free                  | Pure sub-micron ZIF-8 particles (highly agglomerated)    | Water and acetic acid     | [8]              |
| Mechanochemistry                           | ZnO and HmIm powders                                  | Stoichiometric ratio                   | Liquid-assisted-grinding      | Nano-sized ZIF-8 powders (a low degree of agglomeration) | Water                     | <b>This work</b> |

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**Table 2-2 Details for the peak fitting of the Zn 2p<sub>3/2</sub> core level**

| <b>Zn 2p<sub>3/2</sub></b>    | <b>Dry-milled<br/>ZIF-8</b> | <b>Liquid-assisted-milled<br/>ZIF-8</b> | <b>Conventionally synthesised<br/>ZIF-8</b> |
|-------------------------------|-----------------------------|-----------------------------------------|---------------------------------------------|
| Effective maximum<br>position | 1022.28                     | 1022.28                                 | 1022.19                                     |
| Effective FWHM                | 2.07                        | 2.03                                    | 1.91                                        |

**Note:** A Voigt lineshape on a Shirley background was used; a spin-orbit splitting of 23 eV and a doublet ratio of 0.5 were imposed while fitting.

### Derivation of Equation (2-3)

As density ( $\rho$ ), volume ( $v$ ) and surface area ( $A$ ) of a sphere are defined as:

$$\rho = \frac{M}{V} \rightarrow M = \rho * v \quad (2-3.1),$$

$$A = 4 \pi r^2 \quad (2-3.2),$$

$$V = \frac{4}{3} \pi r^3 \quad (2-3.3),$$

$$D = 2r \quad (2-3.4),$$

where  $M$  is the mass (kg),  $r$  is the radius (m), and  $D$  is the diameter (m) of the sphere.

An external specific surface area is defined as:

$$S_{\text{ext.}} = \frac{A}{M} \quad (2-3.5),$$

where  $A$  ( $\text{m}^2$ ) is the surface area.

Using equation (2-3.1) – (2-3.5), the external specific surface area can be expressed as:

$$S_{\text{ext.}} = \frac{4 \pi r^2}{\rho * \frac{4}{3} \pi r^3} = \frac{3}{\rho * r} = \frac{6}{\rho * D} \quad (2-3.6),$$

where the units for  $S_{\text{ext.}}$ ,  $\rho$ , and  $D$  are  $\text{m}^2 \text{kg}^{-1}$ ,  $\text{kg m}^{-3}$ , and  $\text{m}$ , respectively.

When the units for  $S_{\text{ext.}}$ ,  $\rho$ , and  $D$  are converted from  $\text{m}^2 \text{kg}^{-1}$ ,  $\text{kg m}^{-3}$ , and  $\text{m}$ , to  $\text{m}^2 \text{g}^{-1}$ ,  $\text{g cm}^{-3}$ , and  $\text{nm}$ , respectively, the external specific surface area is expressed as:

$$S_{\text{ext.}} = \frac{6000}{\rho * D} \quad (2-3.7).$$

## Chapter Three

### Chemical vapour conversion of ultra-porous ZnO nanoparticle networks to ZIF-8 films for energy applications

#### 3.1 Preamble

The publication relevant to this chapter is “R. Bo\* & M. Taheri\* (co-first author) & B. Liu\*, R. Ricco, H. Chen, H. Amenitsch, Z. Fusco, T. Tsuzuki, G. Yu, R. Ameloot, P. Falcaro, A. Tricoli, Hierarchical Metal Organic Framework Films with Controllable Meso/Macroporosity, *Advanced Science*, Vol. 7 (24), 2020, pp 2002368.” The full publication and its supporting information are presented in Appendix 1.

Dr. Renheng Bo, the candidate (Mahdiar Taheri), and Mr. Borui Liu contributed equally to the published article. Dr Bo and the candidate conceived and designed the research under the supervision of Prof. Antonio Tricoli, Prof. Paolo Falcaro, and A/Prof. Takuya Tsuzuki. Dr. Bo performed the ZnO nanoparticle network synthesis, materials characterizations, and gas phase synthesis of HKUST-1 and MIL-53 (Fe) with the help of the candidate (Mahdiar Taheri). The gas phase conversions of ZnO to ZIF-8 were carried out by the candidate. Mr. Liu designed and performed the electrochemical measurements. Therefore, some parts of this work are published in Dr. Bo’s thesis (The ANU, 2020) under the supervision of Prof. Tricoli.

Other publications built on the knowledge acquired in this work are:

- B. Liu\* & M. Taheri\*, J. F. Torres, Z. Fusco, T. Lu, Y. Liu, T. Tsuzuki, G. Yu, A. Tricoli, “Janus Conductive/Insulating Microporous Ion-Sieving Membranes for Stable Li–S Batteries”, *ACS Nano*, Vol. 14 (10), 2020, pp 13852–13864.
- R. Bo\* & M. Taheri\*, H. Chen, J. Bradford, N. Motta, T. Tsuzuki, P. Falcaro, A. Tricoli, “Paper-Like Writable Nanoparticle Precursor Sheets for Rapid In-Depth Monolithic Metal-Organic Frameworks Patterning”, Under review in *Advanced Functional Materials*.

- B. Liu, R. Bo, M. Taheri, I. Bernardo Di, N. Motta, H. Chen, T. Tsuzuki, Guihua Yu, A. Tricoli "Metal-Organic Frameworks/Conducting Polymer Hydrogel Integrated Three-Dimensional Free-Standing Monoliths as Ultrahigh Loading Li-S Battery Electrodes", *Nano Letters*, Vol. 19 (7), 2019, pp 4391-4399.

### 3.2 Abstract

Three-dimensional structuring of pure metal organic frameworks (MOFs) is a critical requirement for the development of MOF films in numerous applications. In this work, the conversion of highly porous films of ZnO nanoparticles into ZIF-8 films is studied. To comply with the principles of green and sustainable chemistry, the use of toxic and hazardous solvents and the production of harmful by-products are avoided during the conversion; porous films of metal oxide nanoparticles, as green precursors, were converted to pure MOF films via introducing the ligand vapour. The importance of using ligand vapour, instead of ligand solution, to precisely control the film structure and to achieve the full conversion of ZnO to zeolitic imidazolate framework-8 (ZIF-8), is also reported. It was demonstrated for the first time that ZIF-8 films with uniform intergrown grains and structural porosity can be obtained via vapour-phase conversion of the metal oxide precursors. The structure of ZIF-8 films was engineered in a wide range of porosity, from a dense film to a hierarchically porous film, by controlling the reaction temperature. The use of dense and crack-free ZIF-8 monoliths as separators in a model lithium-sulphur battery system resulted in a significant increase in the long-term stability and performance of the battery system over other benchmark separators.

### 3.3 Introduction

#### 3.3.1 MOF films

Metal-organic frameworks (MOFs) made of organic linkers and metal ions have received significant attention due to their diversity, tuneable structure, and remarkably high and uniform micro/mesoporosity [1,2]. Although many reports have investigated various synthesis routes for the production of a powder form of MOFs in the past, the development of the method to produce MOF films is relatively new. A number of methods have recently been explored to fabricate MOF films or membranes on a substrate [1,3,4]. A critical requirement for the development of MOF films is the ability to tailor their structure such as density and hierarchical pores: some applications such as molecular sieving films or gas separation membranes require a dense layer of MOF structures; however, other applications that involve high fluid throughput or adsorption of large molecules call for a hierarchical porous MOF film.

#### 3.3.2 Dense membrane

A dense layer of well-connected crystalline MOFs is of great importance to its applications in molecular sieving and membrane separation. Critical to these applications is the defects and pores in the films; their presence significantly reduces the selectivity of the membrane [5,6]. Recently, MOF-based mixed matrix membranes (MMMs) have been researched extensively for the separation of  $\text{CO}_2/\text{CH}_4$  [7] and  $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$  [8]. However, the selectivity and permeation were negatively affected by the void created during fabrication between polymers and MOFs and the pore-blocking caused by the polymer component [5,6]. Alternatively, *in situ* growth of MOF membrane on a porous support is reported to demonstrate excellent selectivity and high flux [6,9]. Several other strategies such as direct synthesis [10,11], contra-diffusion [12], dip coating [13–15], and chemical vapour deposition [16] are also proposed to synthesise dense MOF films. Although most of these methods are comparably

easy to adapt and simple, it is challenging to obtain a homogeneous membrane on the porous support. This is because of the non-uniform nucleation of MOF on the surface of substrates [17,18].

### 3.3.3 Hierarchical porous film

Recently, there has been extensive research on the fabrication of hierarchically porous MOFs because of their excellent adsorption performance [19,20] and selectivity in catalytic applications [21,22]. There are four approaches to fabricate hierarchical MOF structures with macropores: structural templating, defect formation, use of compressed or supercritical CO<sub>2</sub>, and 3D printing [23]. Structural templating requires “hard” templates such as foams or porous monoliths [24–26] or “soft” templates such as gels or emulsions [27–29], and the crystalline MOFs grow on the surface or around the templates. The templating method is advantageous due to the well-established variety of the templates to be utilised. Due to the difficulty in removing the hard templates, the former method mainly results in composite structures [24,30]. In soft-template methods, insufficient elimination of the sacrificial agents leads to the blockage of MOF pores and subsequent reduction of their performance [23]. Furthermore, the use of sacrificial scaffolds as a template is not desirable from the sustainability point of view. Defect-formation methods involve the introduction of defects in MOF structures during or after MOF synthesis [31,32]. For example, phosphoric acid was used to produce a defective micron-size HKUST-1 by controlling the pH and time of the acid etching [33]. Understanding the stability and behaviour of MOFs in different solvents and various pH ranges is necessary to develop a proper technique to make desired defects. The compressed or supercritical CO<sub>2</sub> method changes the CO<sub>2</sub> pressure in the synthesis chamber to introduce macropores during the direct synthesis of MOFs [34,35]. It was found that a higher pressure of CO<sub>2</sub> results in larger mesopores [36]. It should be noted that most of these methods cannot form controllable monolithic structures [23]. On the other hand, the least-explored 3D-printing methods use MOF-based inks to produce macropores by

combining MOF crystals and binders, and are known to have the ability to precisely control the structure of MOF monoliths [37,38]. It is reported that, in this method, the choice of polymer dictates the hierarchical porosity of the structure and can result in partial/complete pore occlusion of the MOFs [39].

### 3.3.4 Green synthesis

To comply with the principle of green and sustainable chemistry, it is of great importance to minimise or eliminate the use of hazardous reagents and solvents [40]. In this regard, metal oxides/hydroxides such as ZnO/Zn(OH)<sub>2</sub> have advantages over metal salts as raw materials for MOF synthesis; metal oxides/hydroxides are generally less hazardous than metal salts and the reaction by-product is benign water. Metal oxide raw reagents also enable MOF synthesis without the use of organic solvents, additives, or additional extra ligand [41–44].

For example, Li *et al.* converted ZnO nanorods into a dense ZIF-8 membrane by immersing the precursor layer into an aqueous ligand-solution. ZnO nanorods acted as a zinc source and nucleation sites for ZIF-8 crystals to grow into neighbouring crystals to form a thin dense layer. The use of hazardous solvents was avoided, and the synthesis solution was recycled, which made this method environmental-friendly and cost-effective [45].

Another advantage of using metal oxide precursors is that metal oxides can be pre-patterned to serve as a template to form MOF films into desired structures [46,47]. For example, Fischer *et al.* converted pre-deposited and pre-patterned thin films of ZnO and Al<sub>2</sub>O<sub>3</sub> into Zn- and Al-based MOF layers in a microwave vessel [46]. Structural control of MOF films and layers is critical to optimising their performance in applications such as separation and biocatalysis [48–50] and to integrating the films into electronic devices [51].

Recently, the use of ligand vapour to convert metal oxides/hydroxides into MOFs has been demonstrated [52]. Stassen *et al.* formed a dense layer of ZIF-8 from a deposited thin layer of ZnO by reacting the ZnO layer with ligand vapour [16]. However, the conversion reaction

occurred only in the shallow region, within 10 nm from the surface [16]. The use of ligand vapour was applied to the synthesis of other MOFs containing cobalt [53], copper [54,55], and zinc [56]. The use of ligand vapour was also proposed as a solvent-free technique for post-synthesis linker exchange [57].

### 3.3.5 Flame spray technique

Flame spray pyrolysis (FSP) can be utilised to synthesise nanoscale metal oxides and to directly deposit them onto different substrates to form ultraporous nanoparticle network films [58–60]. This method has unique features such as good control over the size of nanoparticles [61], the thickness of deposited films [61,62], and film porosities [61–64], as well as multilayer deposition capability along with a high production rate, scalability, the ability to form patterned films, and a low production cost [65,66]. These features are highly advantageous to form MOF films from metal oxide precursors. As reported elsewhere [16,53,67], the conversion of metal oxide structures to MOF micro-mesoporous structures results in a large volume expansion. FSP can produce metal oxide precursor films with porosities up to 98% that can provide enough space to accommodate the volume expansion. Additionally, FSP can produce small enough particle sizes of the nanoparticle precursors (e.g. less than 20-30 nm for ZIF-8 [16,68]) required for the full conversion of metal oxides.

Despite these advantageous features of FSP methods, the conversion of flame-sprayed ZnO nanoparticle porous layers into ZIF-8 films has not been investigated. In this study, metal oxide nanoparticle porous films have been deposited on different substrates, as a green precursor for MOF-film synthesis. The importance of using ligand vapour, instead of ligand solution, to precisely control the film structure and to achieve the full conversion of ZnO to ZIF-8, is demonstrated. For the first time, by controlling the conversion temperature, pure MOF films with controlled extrinsic porosity (from a dense film to a hierarchical porous structure) were fabricated, without the use of toxic and hazardous solvents and the production of harmful by-products.



It should be noted that the green synthesis of the flame-sprayed ZnO nanoparticle porous layers was outside of the scope of this study.

## 3.4 Experimental Procedure

### 3.4.1 Chemicals

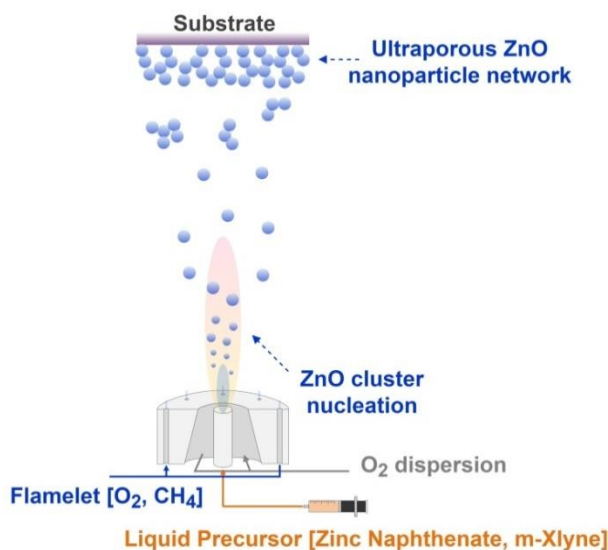
Reagents for the synthesis of ceramic precursors and MOFs were used without further purification. 2-methylimidazole (HmIm, 99 %), trimesic acid (BTC, 95 %), terephthalic acid (BDC, 98 %), M-xylene (99.9 %), and zinc acetate dihydrate (> 98 %) were purchased from Sigma-Aldrich. For liquid precursor solutions, zinc-naphthenate (Zn 10 %), copper-naphthenate (Cu 8 %), and iron-naphthenate (Fe 6 %) were purchased from Strem.

### 3.4.2 Metal oxide nanoparticle network

To produce the ceramic nanoparticle network with controlled particle size and porosity, flame spray pyrolysis (FSP) was conducted using the set-up shown in Figure 3-1. As reported elsewhere [61], zinc-naphthenate precursor solutions in m-xylene with a total metal-ion concentration of  $0.3 \text{ mol L}^{-1}$ , were prepared and combusted in the FSP set-up to produce ZnO nanoparticle networks at a specific height-above-the-burner (HAB) on a variety of substrates. HAB and exposure time of the substrates to the nanoparticle aerosols determine the porosity and thickness of the resulting nanoparticle films, respectively [61,62]. In this work, the effect of lowering the HAB from 20 to 10 cm is discussed. More details on the HAB and exposure time can be found in Appendix 1.

Similarly, to prepare CuO and  $\text{Fe}_2\text{O}_3$  nanoparticle networks, solutions of copper-naphthenate and iron-naphthenate in m-xylene with total metal ion concentrations of 0.2 and  $0.3 \text{ mol L}^{-1}$ , respectively, were prepared, and the nanoparticle aerosols were deposited on substrates at

a HAB of 20 cm. Before the conversion to MOF,  $\text{Fe}_2\text{O}_3$  nanoparticle networks were heat-treated at 450 °C for 5 hours to obtain a pure oxide phase.



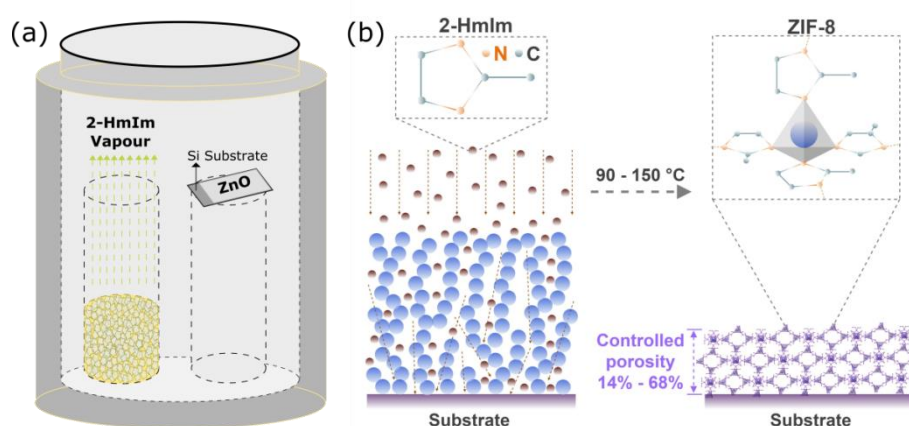
**Figure 3-1 Schematic of flame spray pyrolysis of a zinc precursor and aerosol assembly of an ultraporous ZnO nanoparticle network on a silicon substrate**

### 3.4.3 Vapour Conversion to MOF film

To convert ZnO nanoparticle networks to ZIF-8 films, the as-prepared substrates and 0.5 moles of HmIm ligand powder were placed in a stainless-steel autoclave vial with a Teflon-lining. As shown in Figure 3-2, the substrate and the ligand source were placed with some space between them to avoid direct contact with each other. The autoclave vial was sealed to avoid the leakage of the ligand vapour. Then, the vial was heated at different temperatures (90 - 150 °C) for 18 hours in an oven. Subsequently, the vial was cooled down naturally in the oven.

To convert CuO nanoparticle networks to HKUST-1 films (HKUST stands for Hong Kong University of Science and Technology) and  $\text{Fe}_2\text{O}_3$  nanoparticle networks to MIL-53 (Fe) films (MIL stands for Material of Institute Lavoisier), a two-neck flask was used. The ligands (BTC and BDC solid crystals for HKUST-1 and MIL-53, respectively) were placed at the bottom of the flask and the metal oxide nanoparticle networks deposited on a substrate were hung by a

sample holder, leaving some space between the substrates and ligands. Then, the flask was heated using a Bunsen burner for 15 min. After 15 min, the temperature at the bottom of the flask reached 350 °C; however, the temperature of the substrate is believed to have been less than the decomposition temperature of the MOFs (<300 °C).



**Figure 3-2 Schematic of (a) the vapour conversion chamber; and (b) the reaction between ligand (2-HmIm) and solid precursor (ZnO nanoparticle network) at different temperatures**

Separately, a particulate form of ZIF-8 was synthesised as a comparison to ZIF-8 films. Zinc acetate dihydrate (1 mmol) was dissolved in water (300 mmol) and added to a HmIm (8 mmol) aqueous solution (300 mmol) while being stirred at room temperature. After 2 hours, white ZIF-8 powders were collected by centrifugation. The powders were washed twice with ethanol and dried overnight in an oven (60 °C).

### 3.4.4 Characterizations

X-ray diffraction (XRD) patterns were obtained using a D2 Phaser with a Cu-K $\alpha$  (average wavelength of 1.54059 Å) radiation source (Bruker, USA). The morphology and microstructure of the nanoparticle networks and converted films were analysed by scanning electron microscopy (SEM, Zeiss UltraPlus FESEM, Germany) with an accelerating voltage of 3kV. Samples were sputter-coated with platinum prior to the SEM imaging. Transmission electron microscopy (TEM) and high-angle annular dark-field imaging (HAADF, representing z-contrast) were carried out using a JEOL 2100F FEGTEM (JEOL, Japan) with an

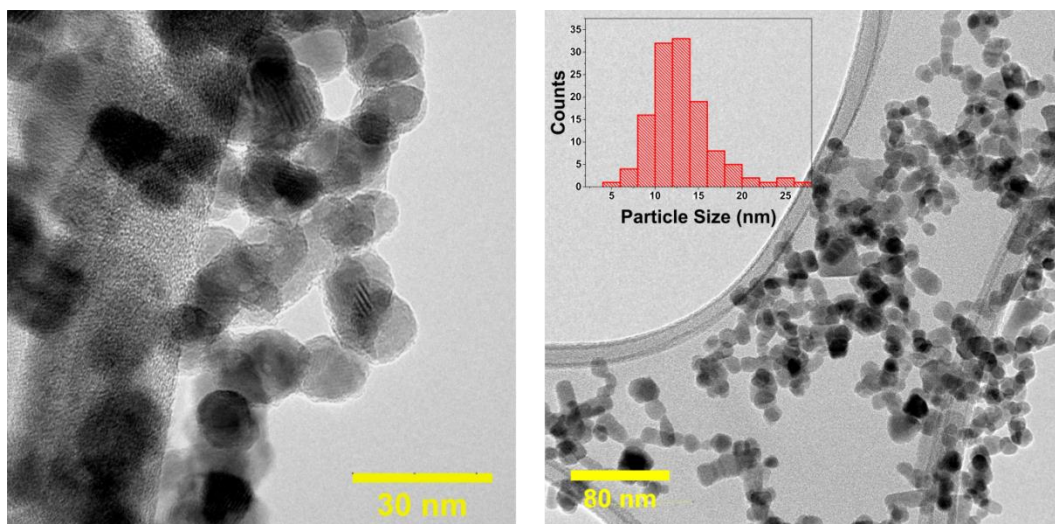
accelerating voltage of 200 kV. To study the conversion kinetic of ZnO nanoparticle networks in the presence of HmIm vapour, synchrotron *in situ* small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) were conducted in a capillary at the AustroSAXS beamline of Elettra Synchrotron (Trieste, IT). The sealed chamber was heated from room temperature (25 °C) to 120 °C with a heating rate of 10 °C min<sup>-1</sup> and was held at 120 °C.

It is noteworthy to mention that the synthesis method to produce ZIF-8 films with controlled extrinsic porosity was repeated at least three times. Characterizations of the samples (XRD and SEM analyses) showed the high reproducibility of the synthesis method.

## 3.5 Results and Discussions

### 3.5.1 ZnO porous films

Past reports [16,68] indicate that the conversion of ZnO to ZIF-8 is localised on the surface of ZnO precursors and is limited to 10-15 nm depth from the ZnO surface [16]. Therefore, for achieving full conversion, it is important to use ZnO precursors with particle sizes less than 20-30 nm. Figure 3-3 shows TEM images of the ZnO nanoparticles collected at a HAB of 20 cm. The size distribution of primary particles was obtained by analysing more than 100 particles in TEM images. As shown in the size distribution histogram in Figure 3-3, the average particle size of the ZnO nanoparticles was 13 nm. Thus, the flame spray pyrolysis method adopted in this study was capable of producing the size of ZnO precursors suitable for the full conversion of ZnO to ZIF-8.

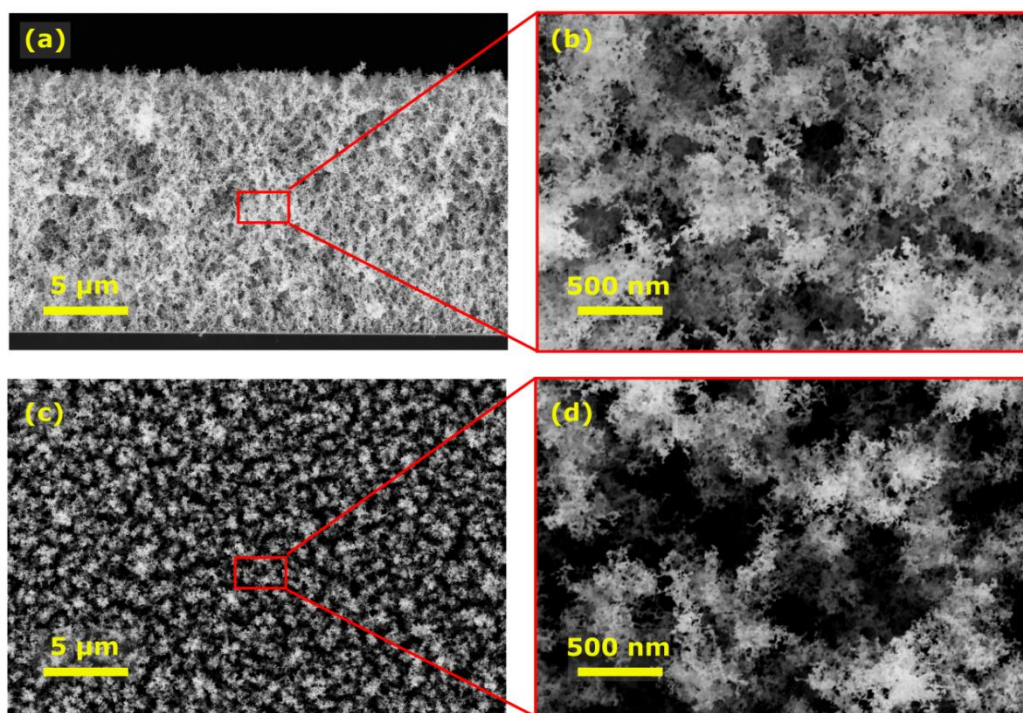


**Figure 3-3** TEM images of the collected ZnO nanoparticles Inset: particle size distribution histogram determined from TEM images; more than 100 particles are counted

Full conversion of ZnO wurtzite crystals ( $5.61 \text{ g cm}^{-3}$  and  $81.4 \text{ g mol}^{-1}$ ) to ZIF-8 ( $0.95 \text{ g cm}^{-3}$  and  $227.6 \text{ g mol}^{-1}$ ) is accompanied by volume expansion by  $\sim 16.5$  times. Therefore, to retain the film thickness before and after the conversion, ZnO nanoparticle network films require an extrinsic porosity of  $\sim 94\%$ . As previously reported, changing the HAB in the flame spray pyrolysis is expected to result in varied extrinsic porosity of the nanoparticle networks [62]. The operation conditions of flame-spray pyrolysis to produce the high extrinsic porosity were investigated as follows.

Two different HABs of 10 and 20 cm were selected to study the effect of extrinsic porosity in the nanoparticle networks on their conversion to ZIF-8 films. The extrinsic porosity of the films was determined by gravimetric and SEM analyses as discussed elsewhere [61,62]. It was found that the nanoparticle networks deposited at HABs of 10 and 20 cm had 90 and 98 % extrinsic porosity, respectively.

Figure 3-4 displays the side views (cross-section) and top views of the ZnO nanoparticle network deposited at a HAB of 20 cm on a silicon substrate. The self-assembly of ZnO nanoparticles resulted in a film of  $\sim 16 \mu\text{m}$  in thickness, consisting of a homogeneous network of nanoparticles on a centimetre-scale base-dimension (up to  $177 \text{ cm}^2$ ).



**Figure 3-4 SEM images of the (a-b) cross-section and (c-d) top view of the ZnO film deposited at 20cm HAB with 98% porosity.**

Lowering the HAB to 10 cm resulted in 90% extrinsic porosity with a homogeneous tree-like structure of ZnO nanoparticles (Figure 3-5). Higher magnification images show that ZnO nanoparticles were partially sintered due to the high temperature of the substrate at this HAB. It was measured that the temperature of the substrate reaches more than 500 °C during the deposition at HAB of 10 cm. The temperature of the exposed surface of the substrate was monitored by a thermometer. Microstructural study and nitrogen adsorption analysis of these nanoparticles in another study [62] revealed that the average primary particle size of the nanoparticle network increased slightly to ~20 nm [62] compared to 13 nm at a HAB of 20 cm (Figure 3-3). However, the primary particle size is still in the range suitable for the full conversion of ZnO to ZIF-8.



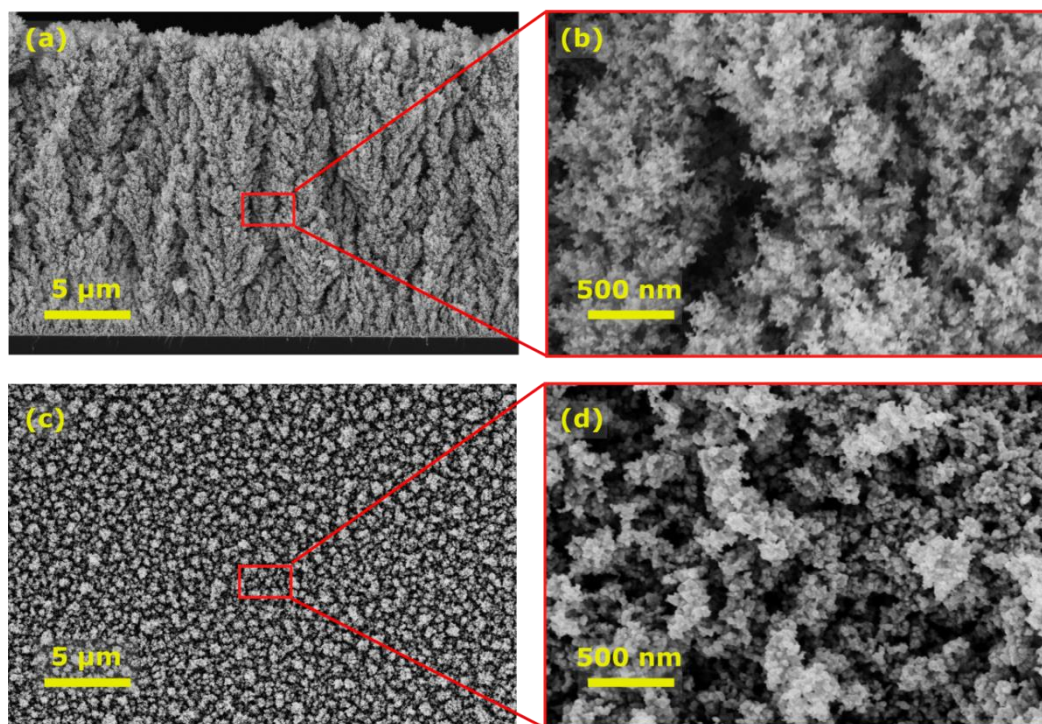
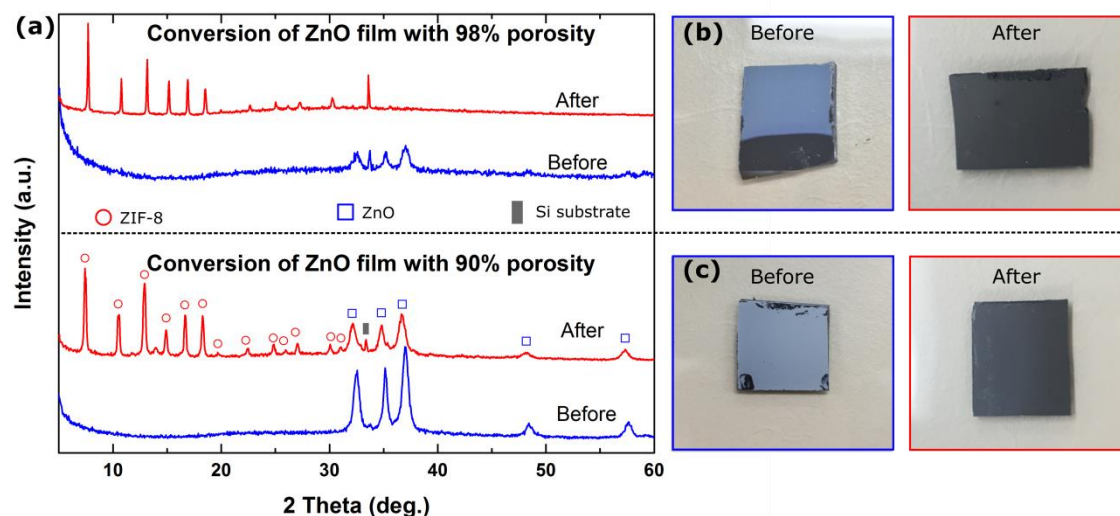


Figure 3-5 SEM images of the (a-b) cross-section and (c-d) top view of the ZnO film deposited at 10cm HAB with 90% porosity.

### 3.5.2 Influence of the extrinsic porosity of precursor films on the conversion

Since the melting temperature of 2-methylimidazole is 142 °C, the nanoparticle networks deposited at different HAB values were converted at 150°C to ensure that sufficient HmIm vapour is generated in the conversion vial. The photographic images of the converted films are shown in Figure 3-6b-c, depicting no visual sign of cracks and inhomogeneity. XRD patterns of the films on a silicon substrate before and after the conversion are shown in Figure 3-6a. The sharp peak at  $\sim 33^\circ$  is associated with the silicon substrate. The formation of ZIF-8 is evident in the XRD patterns of the converted films. In the XRD pattern of the film converted from the ZnO nanoparticle network with 98% extrinsic porosity, the diffraction peaks associated with ZnO were absent. In contrast, the XRD pattern of the film converted from the ZnO nanoparticle network with 90% extrinsic porosity showed both ZnO and ZIF-8 phases, indicating partial conversion of the ZnO nanoparticle network to a ZIF-8 film. This is attributable to the insufficient space in the precursor film (90% extrinsic porosity) to

accommodate the volume expansion, which prevents the further penetration of the Hmlm vapour and progression of the conversion.



**Figure 3-6** XRD patterns and photographs of ZnO films with different porosity (i.e. 90% and 98%) before and after conversion at 150°C for 18 hours. The films were deposited on a Si substrate (ca 1 cm × 1 cm).

It was hypothesised that, an increased conversion temperature leads to an increased vapour pressure of Hmlm in the vial, resulting in a higher driving force of the conversion and higher penetration of the ligand. When the conversion temperature was increased to 180°C for the ZnO film with 90% porosity, the diffraction peaks associated with ZnO wurtzite disappeared (Figure 3-7a), indicative of full conversion of the ZnO nanoparticle network to a ZIF-8 film. However, the converted film showed visual signs of damage caused to the film (Figure 3-7b); cracks were propagated and some parts of the film were chipped off. It is assumed that this damage was caused by the lack of sufficient porosity to accommodate the volume expansion during conversion. The result is in good agreement with the theoretical calculation discussed earlier where an extrinsic porosity of minimum ~94% is required to retain the film thickness before and after the conversion.



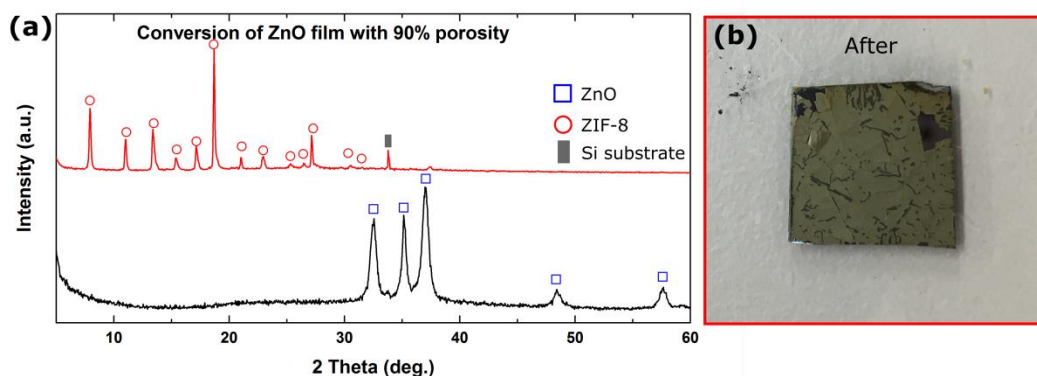
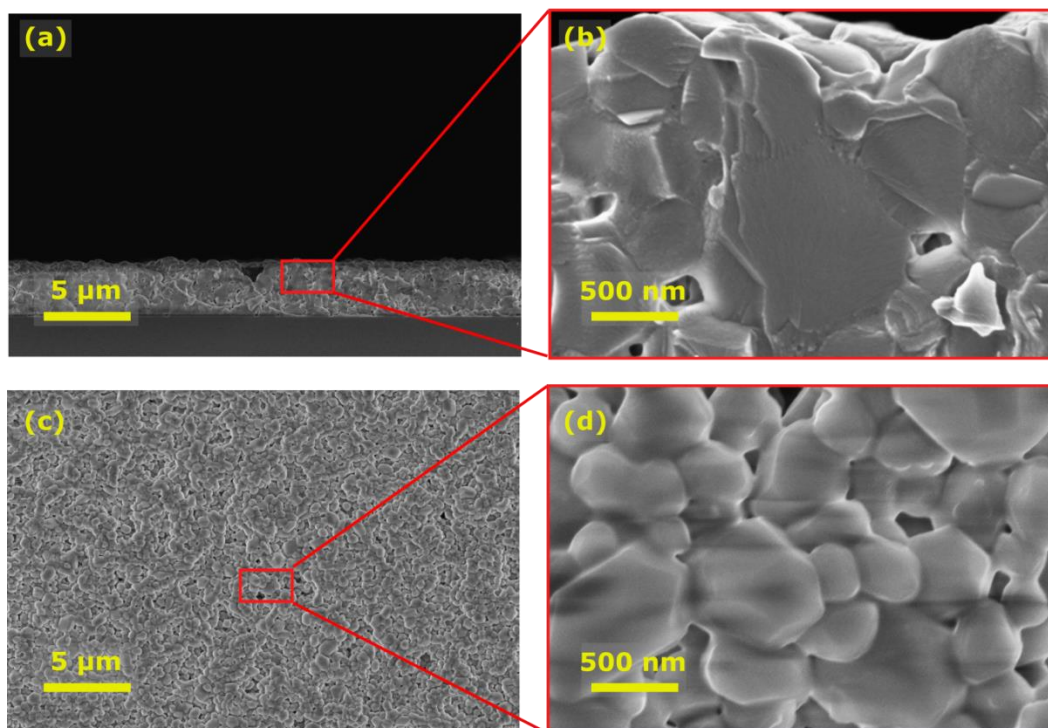


Figure 3-7 XRD patterns of ZnO films with 90% porosity before (bottom) and after conversion at 180°C for 18 hours (top) and its photograph after conversion; The films were deposited on a Si substrate (ca 1 cm × 1 cm).

### 3.5.3 Density of converted films

Figure 3-8 shows the cross-section and top-view SEM images of the ZIF-8 film that was fully converted at 150°C from a ZnO nanoparticle network with 98% extrinsic porosity. The conversion resulted in a re-arrangement of particles and a decrease in film thickness. The SEM images also revealed that the ZIF-8 film had negligible porosity with a couple of micron thickness.



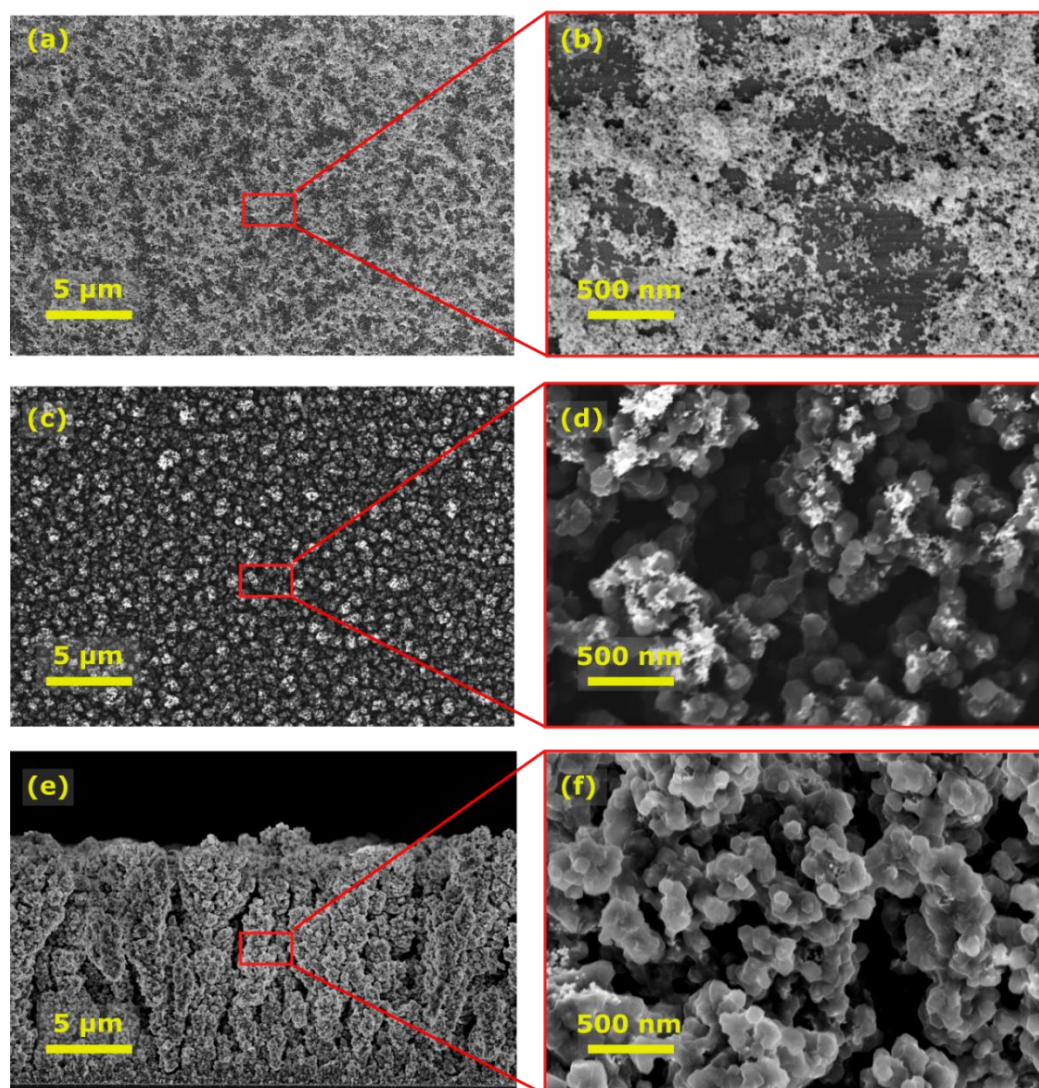
**Figure 3-8 SEM images of (a-b) cross-section and (c-d) top view of the fully converted ZIF-8 film from ZnO film with 98% porosity at 150°C for 18 hours**

### 3.5.4 Liquid-base conversion as an alternative method

Recently, the conversion of metal oxide to MOFs in a liquid solution of the ligand is proposed as a green approach [45,69]. As an alternative method, conversion of the ZnO nanoparticle networks in a liquid phase was investigated in this chapter. ZnO precursor films made using the FSP were immersed in a 0.5M HmIm ethanol solution for 18 hours. It was found that a ZnO nanoparticle network with 98% extrinsic porosity became a non-uniform ZIF-8 film with many isolated islands on the substrate (Figure 3-9a-b). A ZnO nanoparticle network with 90% extrinsic porosity resulted in a homogeneous ZIF-8 film while preserving the tree-like porous structure of the precursor film (Figure 3-9c-f).

It is postulated that ZnO precursor films with 98% porosity are not structurally stable in the ethanol solution due to the loose connection between the nanoparticles and that the fragile network structure collapses when the film is immersed in an ethanol solution of HmIm ligand.

In contrast, the nanoparticle network with 90% extrinsic porosity can survive the immersion step, probably due to the partial sintering of its structure, as previously reported [62].



**Figure 3-9 SEM images of (a-b) top view of ZnO film with 98% porosity; (c-d) top view and (e-f) cross-section of ZnO film with 90% porosity after conversion in an ethanol solution of 2-methylimidazole for 18 hours**

Figure 3-10 shows the XRD pattern of the as-deposited ZnO nanoparticle network with 90% extrinsic porosity films before and after liquid-phase conversion. After conversion, the peaks associated with the ZnO wurtzite structure were present along with those of ZIF-8, indicating that ZnO is only partially converted.

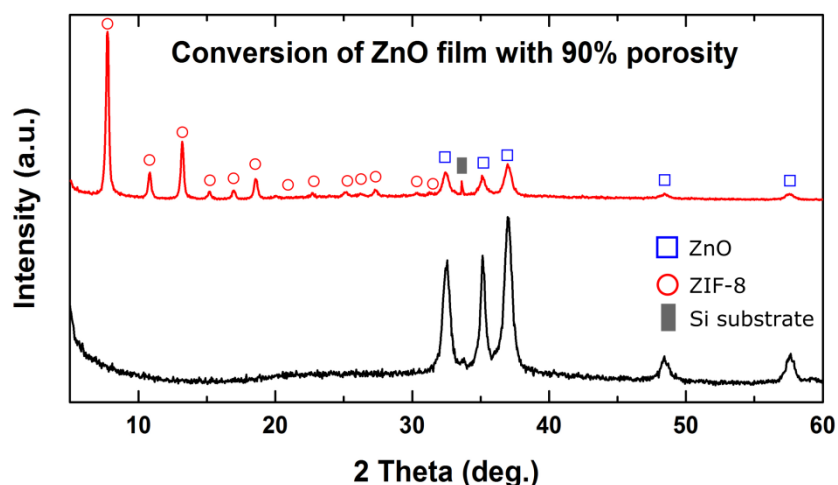


Figure 3-10 XRD patterns of the ZnO film with 90% porosity before (bottom) and after conversion in an ethanol solution of 2-methylimidazole for 18 hours (top); The films were deposited on a Si substrate.

Some particles were removed from the partially converted films and their structure was studied by electron microscopy. The TEM images (Figure 3-11) unveiled that a core-shell structure was formed during the conversion, showing unreacted ZnO cores. It is speculated that, after the formation of ZIF-8 shell around ZnO nanoparticles, further reaction is restricted by the ZIF-8 shell acting as a passivation layer, as discussed in the previous chapter [67, Chapter 2]. These results suggest that the vapour-phase conversion is more effective than the liquid-phase conversion to achieve a full conversion of ZnO nanoparticle networks into ZIF-8 films. Further investigation is required to understand the limitation of the liquid-phase conversion methods by increasing the reaction temperature, changing the solvent, and modifying precursor networks by tuning FSP parameters.



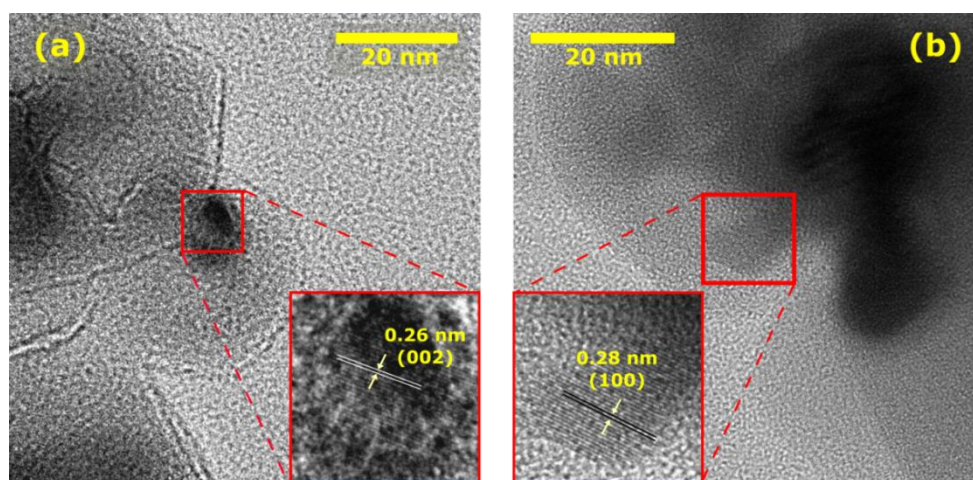
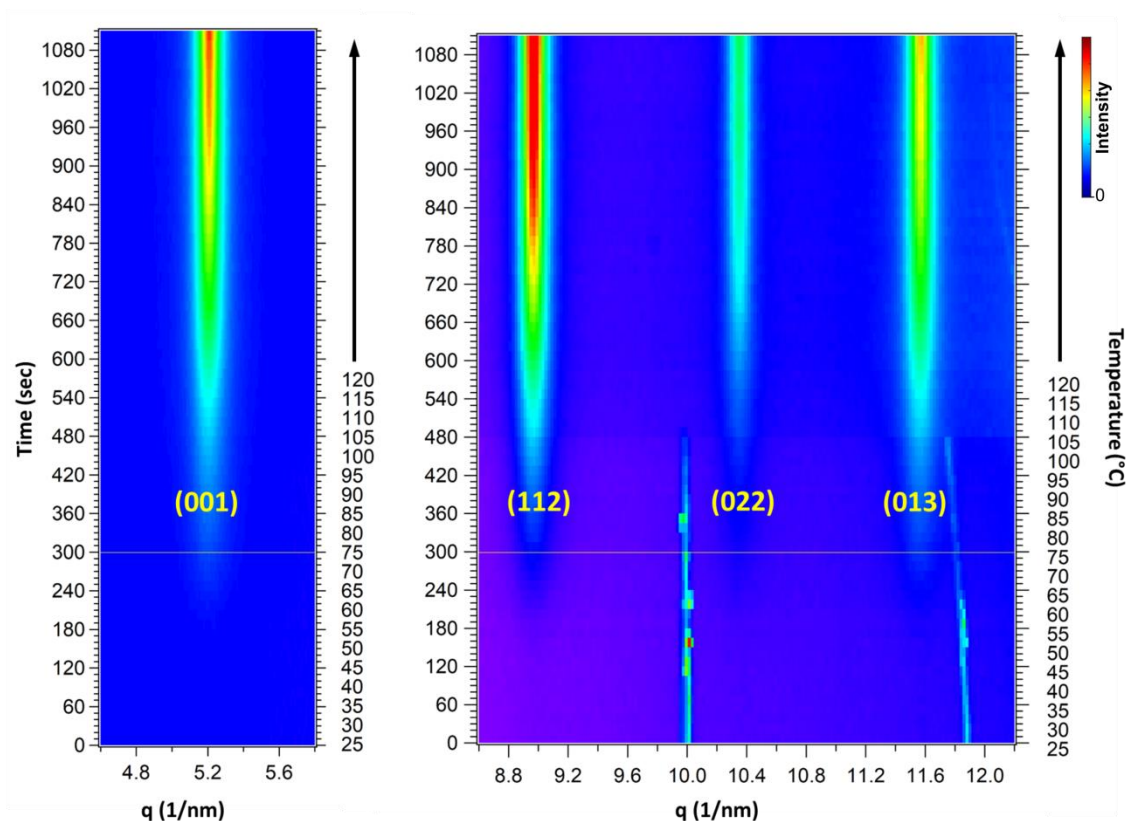


Figure 3-11 TEM images of the ethanol-based conversion of the ZnO film with 90% porosity

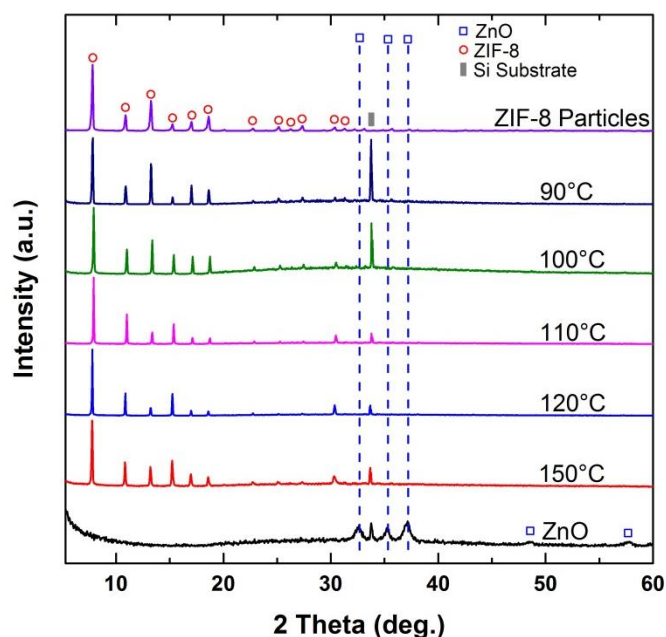
### 3.5.5 Control of extrinsic porosity in resulting ZIF-8 films by changing conversion temperature

To study how the reactivity of HmIm vapour changes as a function of reaction temperature, *in situ* synchrotron small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) were carried out during heating at a constant heating rate. At room temperature, the two peaks in the WAXS pattern (Figure 3-12) at  $q = 10$  and  $11.8 \text{ nm}^{-1}$  are attributed to the crystalline HmIm powders. Increasing the temperature to  $75^\circ\text{C}$  resulted in the appearance of characteristic peaks associated with ZIF-8, at  $q = 5.2 \text{ nm}^{-1}$  in SAXS and  $q = 8.9, 10.4$ , and  $11.6 \text{ nm}^{-1}$  in WAXS. The result suggests that the vapour phase conversion of the ZnO nanoparticle network occurs at much lower temperatures than  $150^\circ\text{C}$  used in the earlier studies in this chapter.



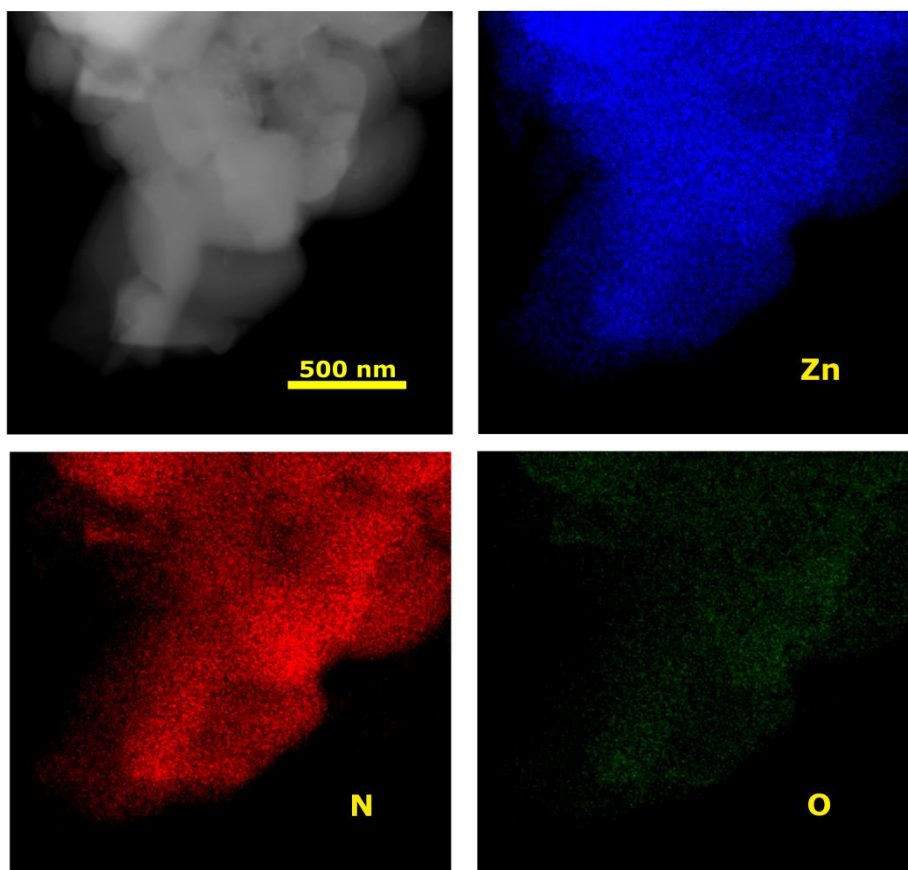
**Figure 3-12** *In situ* SAXS (left) and WAXS (right) data of the conversion of ZnO nanopowders in presence of 2-methylimidazole

The XRD patterns of the samples converted at 150, 120, 110, 100, and 90 °C are shown in Figure 3-13, along with the XRD patterns of an as-deposited ZnO nanoparticle network. The XRD pattern of the ZIF-8 particles synthesised via the aqueous method is also presented in Figure 3-13 as a reference for pure ZIF-8 structure. In all heat-treated samples, only peaks corresponding to ZIF-8 were present, confirming the completion of the full conversion at these temperatures.



**Figure 3-13** XRD patterns of the ZIF-8 films converted at different temperatures, in comparison with that of an as-deposited ZnO film with 98% porosity. The films were deposited on a Si substrate.

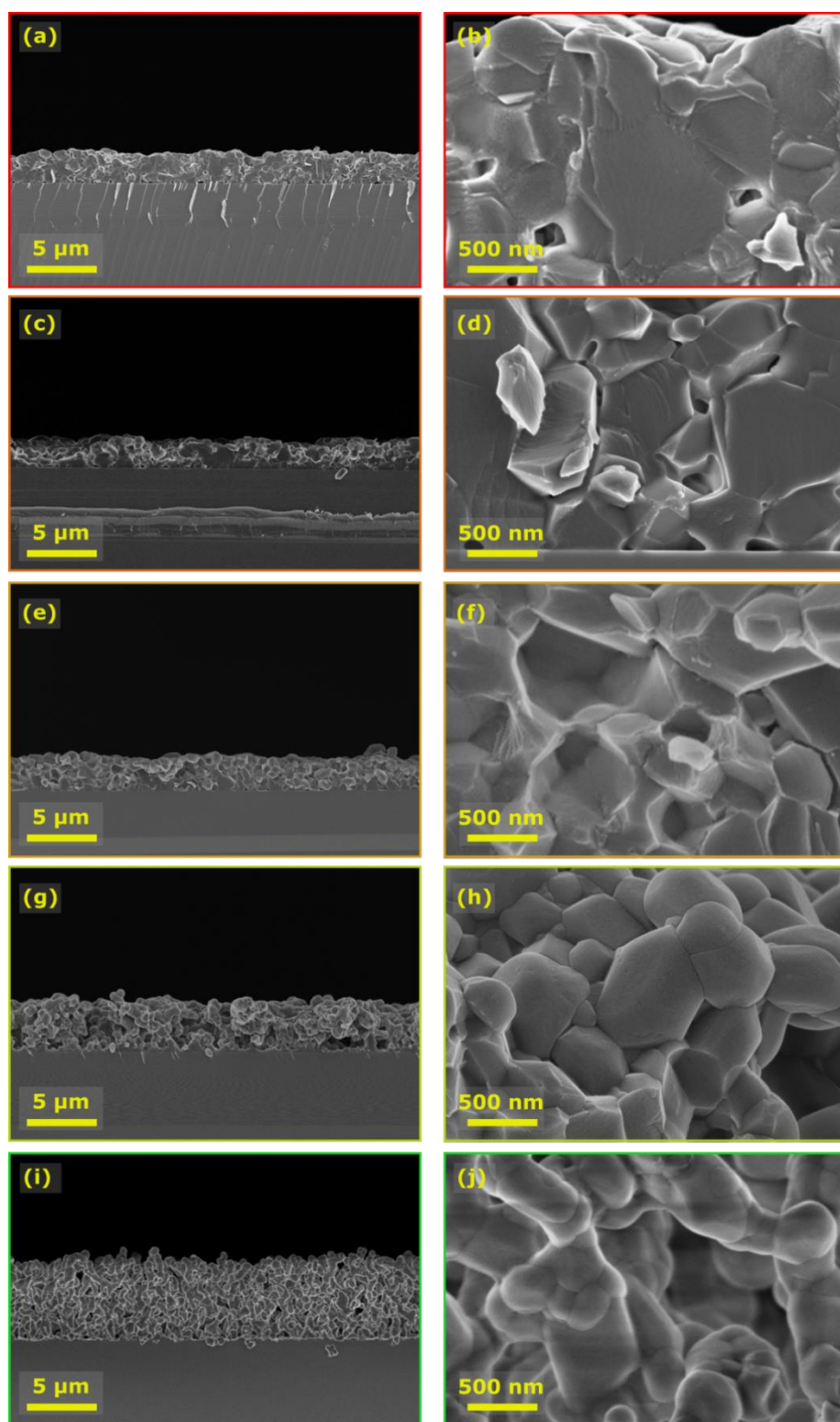
Microstructural TEM studies of the samples at heat-treated 90°C were conducted by detaching ZIF-8 from the substrate and transferring it onto a TEM copper grid. A HAADF image and STEM elemental mapping images are shown in Figure 3-14. The particles did not show core-shell structures, indicating the homogeneous nature of the particles without unreacted ZnO. The elemental maps also showed that zinc and nitrogen (from HmIm) are evenly distributed within the particles and there is no sign of oxygen accumulation that represents unreacted ZnO nanoparticles. The results are in good agreement with the XRD studies.



**Figure 3-14 High-angle annular bright-field scanning transmission electron microscope (HAADF-STEM) and elemental mapping of ZIF-8 particles detached from the film converted at 90°C**

Cross-sectional SEM images of the samples (Figure 3-15) show that ZIF-8 films are less dense when the reaction temperature is lower than 110 °C. Importantly, the sample converted at 90 °C retained its film thickness before and after the conversion (Figure 3-16a-b). Gravimetric and SEM analyses revealed that the conversions at 90 °C resulted in films with 68% external porosity. The value is in reasonable agreement with the theoretical calculation: In a ZnO nanoparticle network with 98% extrinsic porosity, ZnO nanoparticles occupy 2 vol% of the film. When ZnO is converted to ZIF-8 and goes through 16.5 times volume expansion without changing the total volume of the film, the resulting ZIF-8 occupies 33 vol% of the film which is equivalent to 67% extrinsic porosity.

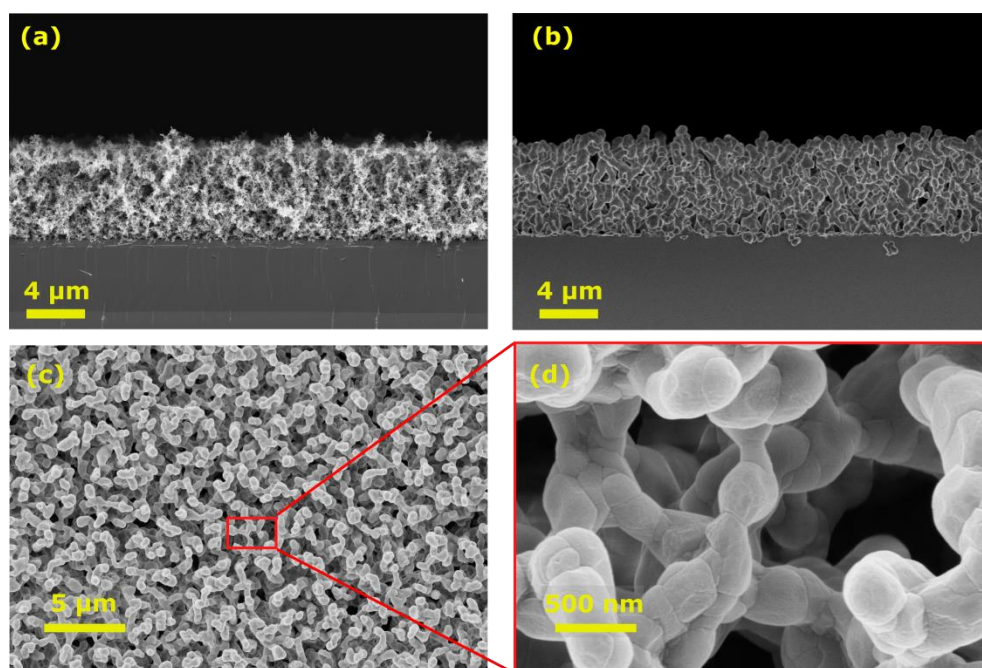




**Figure 3-15** SEM images of the cross sections of ZIF-8 films converted at (a-b) 150, (c-d) 120, (e-f) 110, (g-h) 100, and (i-j) 90°C

Top-view SEM images of the samples converted at 90°C (Figure 3-16c-d) show that the nanoparticle network was homogeneously converted to a ZIF-8 film with micron-sized pores. These macropores (pores larger than 50 nm) in the film consisted of microporous ZIF-8

(having intrinsic pores smaller than 2 nm), thus forming a hierarchical interconnected pore structure in the film.



**Figure 3-16 (a) cross-sectional SEM image of ZnO precursor film in comparison with (b) that of converted at 90 °C, (c-d) top-view SEM images of the ZIF-8 film converted at 90°C showing the connection between ZIF-8 particles and the external porosity of the film**

The metal oxides in precursor films, which act as the nucleation sites, supply metal cations around the parent precursor to form ZIF structures [70]. At low reaction temperatures, the reaction kinetics are slower. This results in fewer disturbances in the original porous structure and more localised conversion of ZnO nanoparticles to ZIF-8 nanoparticles, resulting in the retention of the original film thickness and the formation of a homogeneous hierarchical structure. In contrast, the conversion reaction at higher temperatures leads to the re-arrangement of precursor particles due to faster reaction kinetics, resulting in denser layers.

Since the internal structures of MOFs are micro/mesoporous, the simplest way to produce hierarchically porous MOF structures is by introducing macropores (more than 50 nm) [23]. Hierarchically porous MOF structures have wide-ranging applications [23]. Macropores are vital for many applications where fast access of reactants to the micro-/meso- pores is required, the transportation of large molecules is involved, or fluid penetration with high

throughput is required [23]. For example, Huang *et al.* constructed a hierarchical pore structure by compositing MOFs and a melamine foam with macropores and tested their performance in the catalytic epoxidation of cholesteryl esters [27]. The presence of interconnected macropores in the structure resulted in better accessibility of the catalytic sites and consequently outstanding catalytic performance [27]. Lin *et al.* synthesised a ZIF-67/melamine-sponge composite using a dip-coating method and surfactant modification of the sponge [71]. The composite structure with macropores exhibited a very high adsorption capacity of large pollutant molecules (i.e. malachite green dye) [71].

Furthermore, the retention of the film thickness and precise positioning of MOFs are vital in device fabrication (such as bioreactor, electronic, sensing devices), as they allow better control over the device structure [72]. The controlled conversion of ZnO precursors to hierarchical ZIF-8 films proposed in this study, can be utilised to make devices such as bioreactor and biosensing devices with high accuracy where high fluid circulation and large molecule accommodation are required.

### 3.5.6 Collaborative works

Since this work was done in collaboration with Prof. Antonio Tricoli's group (ANU), the details of the following topics are discussed in Dr. Bo's thesis (ANU, 2020) and presented in Appendix 1.

#### 3.5.6.1 Synthesis

It is demonstrated in Appendix 1 that the thickness of the dense ZIF-8 films can be precisely controlled by changing the deposition time of ZnO nanoparticle films. Cross-sectional SEM images showed that the thickness of the dense ZIF-8 films varied from 80 nm to 230  $\mu\text{m}$  (ranging over four orders of magnitude).

Considerable research activities have been devoted to achieving high selectivity in gas separation using well-defined ZIF structures, by taking advantages of ZIF's suitable pore size and molecular sieving effects [9,73–75]. It is well documented in the literature that, for this application, it is of great importance to synthesise dense layers of MOFs without using binders [73,74]. Various synthetic strategies have been proposed to achieve this goal, including direct synthesis on porous substrates and the formation of polymer composites (i.e. mixed matrix membrane). However, it is proved to be challenging to achieve a homogeneous thick layer in the former strategy and very high loading of MOFs in the latter [9,73–75]. In this collaborative chapter, vapour phase conversion of metal oxide nanoparticle networks is proposed as a new approach to synthesise binder-free ZIF-8 dense layers with controlled thickness.

In this collaborative chapter, it is also demonstrated that ZnO-nanoparticle networks can be deposited on different materials (including steel, aluminium, and zirconia) with different geometries (spherical, curved, and cylindrical). Subsequently, they were successfully converted to dense ZIF-8 films. Furthermore, the ZnO-nanoparticle network was deposited on a large glass-fibre filter-paper with a diameter of 15 cm and converted to ZIF-8 in a specialised reaction chamber.

It was found that dense ZIF-8 films are mechanically strong enough to be detached from the silicon substrate and be stand-alone films when they have tens of micrometre thickness. To facilitate the detachment, a double layer strategy was developed in which a layer of  $\text{SiO}_2$  nanoparticle network was deposited prior to the deposition of ZnO nanoparticle networks, as a mechanically weak sacrificial layer. During the conversion of ZnO into ZIF-8,  $\text{SiO}_2$  layer did not react with HmIm vapour and remained mechanically fragile, thus, little force was required to detach ZIF-8 film from the silicon substrate.

Finally, to generalise the applicability of the vapour phase conversion of metal oxide nanoparticle networks to other MOF films, it was demonstrated that CuO and  $\text{Fe}_2\text{O}_3$

nanoparticle networks with 98% porosity were successfully converted to pure HKUST-1 and MIL-53 films.

### 3.5.6.2 Applications

Molecular sieving properties of the self-standing dense ZIF-8 films were assessed by assembling it in a Lithium-Sulphur (Li-S) battery as a separator. These rechargeable batteries offer a high theoretical capacity and energy density [76,77]. A major obstacle in the development of Li-S battery technology is the migration of soluble polysulphides to the Li electrode through commercial separators, which results in a rapid decay in their capacity [78,79]. It was assumed that a dense layer of ZIF-8 structure with microporosity (pore opening of 0.34 nm [80]) can stop the migration of polysulphides ( $>0.5$  nm) while permitting diffusion of lithium cations ( $\leq 0.1$  nm). The battery cell assembled using a ZIF-8 dense layer demonstrated a high initial capacity and a small degradation per cycle, comparing with battery cells with benchmark separators (Appendix 1). The result shows that the dense layer of ZIF-8 film with intrinsic microporosity was capable of blocking destructive polysulphide relocation to the Li electrode.

In another study, a similar vapour conversion approach was adopted to convert thin layers of metal atoms (Zn and Co), which were chemically bonded on graphene surfaces, to ZIF-8 and ZIF-67 [81]. This resulted in a thin conformal layer of high-aspect-ratio metal-organic-frameworks (HAR-MOFs) on graphene sheets which were used as ion-sieving separators in Li-S batteries. Results showed that the separators were highly efficient in blocking soluble polysulphides from travelling to the Li electrode and the battery retained a high capacity of ~75% after 1700 cycles.

## 3.6 Conclusions

In this study, a flexible and green strategy to form three-dimensional structures of MOF films is presented. In this approach, highly porous films of ZnO nanoparticles were fully converted

to uniform ZIF-8 films with intergrown grains. The extrinsic porosities of the ZIF-8 films were tuneable, from a dense film to a hierarchically porous film. This was achieved by controlling the reaction temperature in the vapour-phase conversion of the metal oxide precursor (90 to 150 °C). Other unique advantages of this method include structural homogeneity, high scalability, and designable geometrical features. Using this method, dense films of ZIF-8 with intergrown grains were fabricated as robust self-standing monoliths without the need for binders. The ZIF-8 monoliths were tested as separators in lithium-sulphur batteries. Replacement of commercial polymeric separators with the ZIF-8 monolith resulted in enhanced long-term stability and performance of the batteries. The result showed that the crack-free ZIF-8 monolith (pore opening of 0.34 nm) is capable of blocking the migration and deposition of polysulfide species ( $>0.5$  nm) while permitting diffusion of lithium cations ( $\leq 0.1$  nm) (molecular sieving effect).

The approach to engineer the structure of MOF films demonstrated in this study can provide new directions for the design and fabrication of binder-free-MOF films with controlled extrinsic porosities and thicknesses on different substrates. Hierarchically porous MOF films with interconnected meso-/macro- pores ( $>2$  nm) in their structure can be utilised in many applications where large molecules are involved or fluid penetration with high throughput is required. Dense and crack-free films are of great importance to applications in molecular sieving and membrane separation.

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## Chapter Four

### Water stability of cobalt doped ZIF-8: A quantitative study using optical analyses

#### 4.1 Preamble

The publication relevant to this chapter is “M. Taheri, T. G. Enge, T. Tsuzuki, Water stability of cobalt doped ZIF-8: A quantitative study using optical analyses, Materials Today Chemistry, Vol. 16, 2020, pp 100231.” The relevant supporting information is presented in Section 4.8.

The following publication is an extension to the investigation of the water stability of ZIF-8 powders and is not presented in this thesis:

- M. Taheri and T. Tsuzuki, “Photo-accelerated hydrolysis of metal organic framework ZIF-8”, ACS Materials Letters, Vol. 3, 2021, pp 255–260.

#### 4.2 Abstract

Zeolitic imidazolate frameworks (ZIFs), in particular ZIF-8 (made of  $\text{Zn}^{2+}$  and 2-methylimidazolate) and cobalt-doped-ZIF-8, are found important for many energy and environmental applications. It was reported that ZIFs show excellent structural stability in water and thus ideal for aqueous applications. However, recent studies also found some evidence that ZIF-8 undergoes hydrolysis in water. Despite the importance of ZIF's stability in many aqueous applications, the extent of ZIFs' degradation in water is still not yet fully understood. This work reports a quantitative study of the water stability of 0-100 at% cobalt-doped ZIF-8, using a new combination of analytical tools. The study demonstrated the importance of analysing both filtered powders and the filtrate liquid systematically, in particular by using UV-Vis spectroscopy and thermogravimetric analysis. The combination of analytical tools allowed the study on the effects of ZIF concentrations in water, cobalt doping

levels, and amounts of ligands in water on the water stability of ZIF samples. The effect of cobalt-doping was investigated by using ZIF particles with identical sizes (200-400 nm), in order to eliminate the effects of particle size on hydrolysis. Unlike other synthesis methods, a mechanochemical ball milling method allowed the production of nano-scale ZIF-8 particles with similar sizes, independent of cobalt-doping levels. The proposed combination of analytical tools including UV-Vis spectroscopy can be applied to the study of the water stability of other MOF materials.

### 4.3 Introduction

Zeolitic imidazolate frameworks (ZIFs), a subclass of metal organic frameworks (MOFs), consist of tetrahedral transition metal ions bridged by imidazole derivatives. Due to their reported thermal and chemical stability, they have been extensively researched for a variety of applications in membranes [1,2], batteries [3], CO<sub>2</sub> capture [4], and gas sensing [5]. The water stability of ZIFs is of significant importance to aqueous applications including water purification [6,7], biological [8,9], and catalytic [10–12] applications.

ZIF-8, made of Zn<sup>2+</sup> and 2-methylimidazolate, is known as one of the most thermodynamically water-stable MOFs [13]. Its water stability has been experimentally demonstrated, mainly using powder X-ray diffractometry (XRD), surface area analysis, and electron microscopy. The stability of ZIF-8 in boiling water was first reported in 2006 by Park *et al.* using XRD [14], and subsequently in 2011 by Pan *et al.* [15]. In 2009, Low *et al.* demonstrated that ZIF-8 has higher steam stability than other MOFs including Al-MIL-110, MOF-74, and -MIL-101 [16]. Many reports used ZIF-8 in aqueous applications and did not detect any structural change before and after the tests [17,18].

However, recently, the instability of ZIF-8 in water has started to attract attention. In 2010, Cychosz and Matzger showed that ZIF-8 is stable in water only kinetically and its structure is lost after immersion in pure water for three months [19]. In 2013, Liu *et al.* documented the

hydrolysis of ZIF-8 under hydrothermal conditions (80°C for 24 h) for the first time. Using scanning electron microscopy (SEM) and XRD studies, they showed that the hydrolysis depends on ZIF-to-water ratios and that adding extra 2-methylimidazole (HmIm) can prevent the hydrolysis [20]. Zhang *et al.* used inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis of the filtrate to observe the continuous release of  $\text{Zn}^{2+}$  from a ZIF-8 membrane during water pervaporation through the membrane [21]. More recently, Sheng *et al.* observed that water immersion of ZIF-8 induces changes in crystallinity and the formation of new unknown XRD phases [22]. Some efforts in improving the water stability of ZIFs were made by imparting surface hydrophobicity of ZIF particles [20,23,24]. The water-stability of ZIF-8 powders in the presence of different anions, instead of pure water, was studied by Wang *et al.* [25]. A detailed study on the degradation of ZIF-8 in phosphate buffered saline (PBS) media confirmed the formation of zinc phosphate particles after immersion in PBS 10 mM [26]. Luzuriaga *et al.* conducted a similar study and reported that ZIF-8 degrades in buffer solutions and cell media; however, based on XRD and SEM analyses, they still concluded that ZIF-8 is stable in pure water [27].

Very recently, Zhang *et al.* argued that the conflicting results on the water stability of ZIF-8 in the literature are due to the fact that different methods (i.e. filtration or centrifuge) were used to collect ZIF-8 particles after immersion tests [28,29]. In their study, they collected ZIF-8 powders after immersion for 24 hours, by evaporating the water. Then they analysed the collected powder using XRD and SEM analyses along with nitrogen adsorption isotherms, to quantify the degradation degree of ZIF-8 in water and concluded that ZIF-8 is not stable in pure water under ambient conditions [28]. However, the study did not consider the possibility of the formation of precipitates during drying, which would interfere with the interpretation of their results.

For the successful water-related applications of ZIFs, it is vital to know their chemical stability in water. However, the past studies showed conflicting results. In addition, most of

the past studies on the water-stability of MOFs have relied on XRD, electron microscopy, or recently surface area analysis, which are not sensitive to the partial hydrolysis of MOF structures. As such, the extent of ZIFs' degradation in water has not been fully understood yet.

This chapter reports a new combination of analytical tools to quantitatively determine the water stability of ZIF materials. The study highlights the importance of analysing both filtered powders and the filtrate liquid systematically, as each will provide critical information about the water stability of ZIF structures. In particular, the study demonstrates for the first time that UV-Vis absorbance spectroscopy of the filtrate and thermogravimetric analysis (TGA) of the filtered powders can be combined with XRD, electron microscopy, nitrogen adsorption isotherms, and inductively coupled plasma mass spectrometry (ICP-MS), to quantitatively study the hydrolysis of ZIF-8 and cobalt-doped-ZIF-8 powders accurately. The new combination of analytical tools enabled us to quantitatively study the effect of ZIF concentration in water and also to determine the amount of HmIm required to prevent the hydrolysis of ZIF structures.

In addition, the effect of cobalt doping on the stability of ZIF-8 is investigated. ZIF-67 is structurally identical to ZIF-8 but  $\text{Zn}^{2+}$  is replaced with  $\text{Co}^{2+}$ . ZIF-67 has a bandgap energy in the visible light range (1.98 eV) and hence it is considered as a new class of photocatalysts that have important applications in environmental remediation including heavy metal scavenging from water and  $\text{CO}_2$  reduction [30,31]. In ZIF-8, zinc ions can be substituted by cobalt ions at any ratio from 0 to 100%. Mixed metal ZIF-8 has different physicochemical characteristics compared to ZIF-8 and ZIF-67 [32–34]. For example, cobalt-doped ZIF-8 shows enhanced  $\text{CO}_2$  and  $\text{H}_2$  uptakes and catalytic  $\text{CO}_2$  conversion rates, as compared to ZIF-8 and ZIF-67 [34]. Therefore, it is important to study the water stability of ZIF-67 as well as the effect of cobalt doping on the stability of ZIF-8.



It is reported that smaller particle sizes of ZIFs lead to faster decomposition [26]. Thus, in order to study the effect of cobalt doping on the stability of ZIF-8, it is necessary to avoid the effect of particle size on water stability. For this, ZIF samples with different cobalt doping levels should have similar particle sizes. The size of ZIF powders can be influenced by synthetic conditions including solvent types, temperature, and the concentration of the metal-ligand-solvent [35,36]. Zareba *et al.* [33] prepared cobalt-doped-ZIF-8 particles (0-100%) by substituting zinc nitrate with cobalt(II) nitrate, which resulted in the increased particle size with increasing amount of cobalt, from 20 (for ZIF-8) to over 500 nm (for ZIF-67) in diameter. To date, there was no report demonstrating the single method that enables the preparation of ZIF particles with similar sizes for a wide range of cobalt-doping levels.

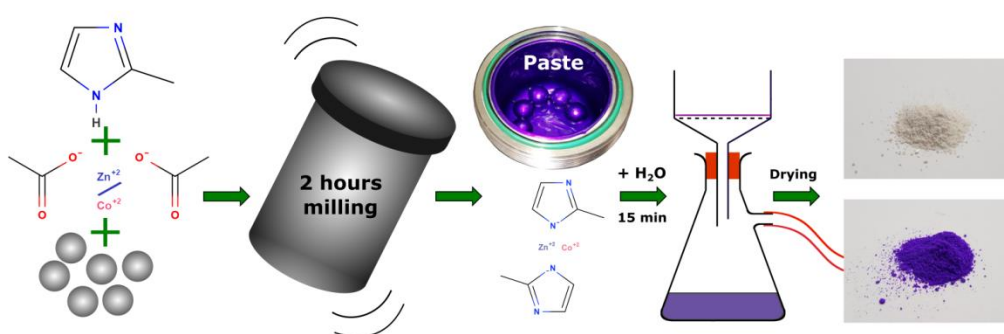
This chapter demonstrated a new synthesis method that allows the formation of similar sizes of ZIF powders irrespective of cobalt-doping levels. A mechanochemical method using a ball mill was developed, which allowed the synthesis of ZIF powders in the range of 200-400 nm, independent of cobalt concentration. Ball milling provided additional benefits such as scalability, waste minimisation by allowing minimum use of extra ligand, and solvent-less processing for environmental benefits [37,38]. Only metal salts and 2-methylimidazole were used as starting reagents.

## 4.4 Experimental

### 4.4.1 Synthesis of cobalt-doped ZIF-8

Cobalt acetate (pink colour), zinc acetates (white colour) and 2-methylimidazole (HmIm, white colour) were purchased from Sigma-Aldrich. The schematic of the synthesis procedure is shown in Figure 4-1. First, the reagents with a metal-to-ligand molar ratio of 1:8 were placed in a ball milling vessel made of stainless steel, along with stainless steel balls of 8 mm in diameter. A ball-to-powder mass ratio of 10:1 was used throughout the experiments.

The total molar amounts of metal acetates and HmIm in one batch of milling were fixed to be 2.08 and 16.6 mmol, respectively. Milling was performed in a Spex 8000 mixer/mill for 2 hours. The milling resulted in a homogenous paste. The colour of the paste was clear with zinc acetate and purple in the presence of cobalt acetate. In the next step, 25 mL of deionised (DI) water (18M $\Omega$ ) was added into the milling vessel and shaken. After 15 minutes, the paste turned into a wet powder. The resulting powder was vacuum-filtered using filter paper with an average pore size of 200 nm. The powders were washed with DI water and then with ethanol to remove unreacted reactants, followed by drying at 50°C in air overnight. The powder samples were also heat-treated at 150°C for 2 hours to drive out guest molecules trapped in the pores of ZIF cages. The samples were denoted according to their nominal cobalt content in atomic %, as ZIF-8 (no cobalt), 30%Co-ZIF-8, 50%Co-ZIF-8, 70%Co-ZIF-8, and ZIF-67 (no zinc). The Co concentrations in the resulting samples were measured using scanning electron microscopy-energy dispersive X-Ray spectroscopy (SEM-EDS) and inductively coupled plasma - optical emission spectroscopy (ICP-OES, 5110 SVDV, Agilent, USA).

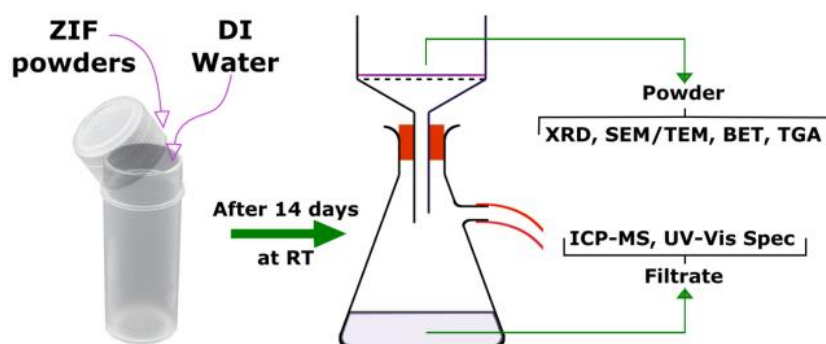


**Figure 4-1 Schematic of the synthesis procedure of cobalt-doped-ZIF-8 powders.**

#### 4.4.2 Study of water stability

The water stability of thus synthesised ZIF powders was studied in DI water (18M $\Omega$ ) at room temperature for 14 days. The specimen was kept in the dark for the whole duration to avoid possible photolysis. Different powder-to-water mass ratios of 0.75, 1.5, 3, and 6 wt% were chosen. To study the effects of cobalt doping level on the water stability, a powder-to-water mass ratio of 3 wt% was used.

After certain durations of immersion in water, the ZIF powders were filtered using a 200 nm syringe filter. Both filtered powders and the filtrate liquid were systematically analysed, as shown in Figure 4-2.



**Figure 4-2 Schematic of the water stability test and characterization methods on the filtered powders and filtrate liquid.**

The crystallinity of the powders was analysed by Powder XRD using a D2 Phaser (Bruker, USA). SEM (Zeiss UltraPlus FESEM, Germany), transmission electron microscopy (TEM, JEOL 2100F FEGTEM, Japan), and scanning transmission electron microscopy with X-ray energy dispersive spectrometry (STEM-XEDS, JEOL 2100F FEGTEM, Japan) were utilised to probe the morphology and elemental mapping of the powders with accelerating voltage of 2 and 200 kV, respectively. Prior to SEM analysis, platinum coating was applied to the powder. TGA was performed on ZIF powders using a Netzsch STA 449 F3 in air in an alumina crucible. Nitrogen adsorption isotherms at liquid nitrogen temperature were collected using a Tristar II 3020 (Micromeritics, USA). Specific surface areas were calculated

using the Brunauer–Emmett–Teller (BET) model ( $S_{\text{BET}}$ ) and Langmuir model ( $S_{\text{L}}$ ), in the pressure range of 0.23 and 60 mmHg for  $S_{\text{L}}$ , and  $P/P_0$  of 0.001 and 0.05 for  $S_{\text{BET}}$ , where  $P$  is the pressure and  $P_0$  is  $\sim 715$  mmHg. Prior to the surface area measurements, samples were degassed under vacuum at  $120^\circ\text{C}$ . UV-Vis absorbance spectra of the filtrates were recorded in the wavelength range of 190–800 nm using a Cary 60 UV-Vis spectrophotometer (Agilent, USA). Concentrations of released zinc and cobalt cations in the filtrates were determined using an iCAP-RQ quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS) instrument (Thermo Scientific, USA): A multi-element standard external calibration curve was utilised to measure the concentrations of zinc and cobalt, while long-term instrument drift was monitored using a 100 ppb Y internal standard solution.

#### 4.4.3 Stabilization by addition of extra ligand

To study the effect of extra HmIm in water on the stability of the ZIF structures, ZIF-67 powders were dispersed in water at 3 wt% concentration. The ZIF-67 to HmIm molar ratios of 1:0, 1:0.1, 1:0.25, 1:0.5, 1:1, 1:2, 1:4, 1:6, and 1:8 were studied.

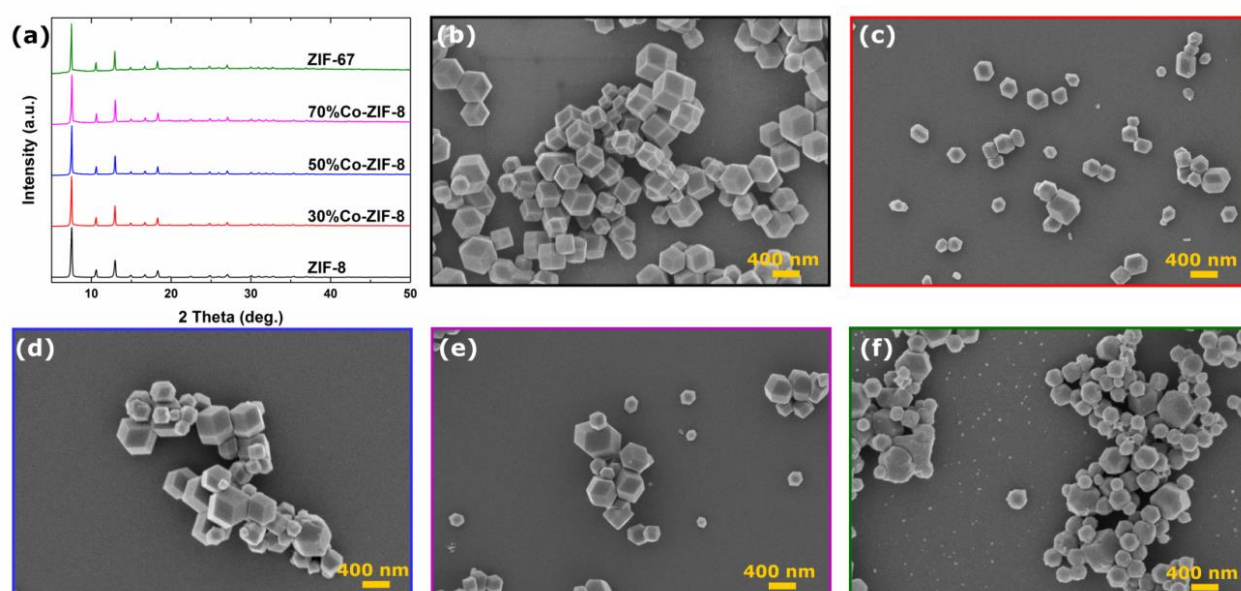
### 4.5 Results and discussion

#### 4.5.1 Synthesis of cobalt-doped ZIF-8 powders

Figure 4-3a shows XRD patterns of ZIF-8 and cobalt-doped ZIF-8 before water immersion. All diffraction peaks coincide with those of ZIF-8 and ZIF-67 with a sodalite (SOD) topology [14] and no changes are observed with increasing cobalt content. After ball milling of the mixed powders of zinc and/or cobalt acetate and HmIm (molar ratio of 1:8) without any solvent, a viscous paste was obtained. The FTIR spectra (Figure S 4-1) of the paste indicate that the paste consisted of  $\text{Zn/Co}(\text{HmIm})_2$  coordination and excess HmIm. When water is added, the excess HmIm acted as a deprotonating agent to form ZIF crystals in water [36]. The metal-acetate-to-HmIm molar ratio of 1:8 is lower than any molar ratios reported for the

successful synthesis of SOD-ZIF-8 using water [36]. When the metal-acetate-to-HmIm molar ratio was reduced to 1:4, the so-called dia-structure of ZIF-8, that has a diamond topology with a higher density and a smaller pore volume than SOD-ZIF-8 [39,40], was formed (Figure S 4-2).

Figure 4-3b-f depict typical SEM images of the as-synthesised ZIF-8 and cobalt-doped ZIF-8. The SEM images show particles with well-defined geometrical-shapes. Particle sizes were in the range of 200-400 nm for all cobalt-doped samples, regardless of their cobalt doping levels. In contrast, when ZIF powders were synthesised by mixing aqueous solutions of zinc acetate and 2-methylimidazole, without a mechanochemical ball milling step, their size increased as cobalt doping level increased (Figure S 4-3), which is similar to the results of Zareba *et al.* [33]. The difference in resulting particle sizes between the two methods is likely due to the difference in nucleation and growth conditions. It is speculated that, the presence of  $\text{Zn/Co(HmIm)}_2$  in the milled sample leads to a faster nucleation rate of ZIF particles than in the direct aqueous precipitation method, by  $\text{Zn/Co(HmIm)}_2$  acting as nucleation sites of ZIF crystals.



**Figure 4-3 (a) XRD patterns and (b-f) SEM images of (b) ZIF-8, (c) 30%Co-doped-ZIF-8, (d) 50%Co-doped-ZIF-8, (e) 70%Co-doped-ZIF-8, and (f) ZIF-67.**

The concentration of cobalt in the doped samples (i.e. 30%Co-, 50%Co-, and 70%Co-doped-ZIF-8) was measured using SEM-EDS and ICP-OES (Figure S 4-4). It was found that the cobalt concentrations in the ZIF structures are slightly higher than the nominal values, which is similar to the results in the literature [33,34].

Figure 4-4a shows STEM elemental mapping images of 50%Co-ZIF-8. A high-angle annular dark field STEM image (HAADF, representing a Z-contrast image) is also shown in Figure 4-4a. It is evident that carbon, zinc, and cobalt are all evenly distributed within the particles. All particles contain zinc and cobalt. No separate particle containing only cobalt or zinc, was evident. The results demonstrate the successful production of solid solutions of ZIF-8 and ZIF-67 using ball milling.

Figure 4-4b depicts the nitrogen adsorption isotherms of undoped and cobalt doped ZIF-8. ZIF-8, 30%Co-ZIF-8, 50%Co-ZIF-8, 70%Co-ZIF-8, and ZIF-67 had BET surface areas of 1881, 1752, 1665, 1662, and 1525  $\text{m}^2 \text{g}^{-1}$  and Langmuir surface areas of 1998, 1885, 1782, 1776, and 1628  $\text{m}^2 \text{g}^{-1}$ , respectively. There was a slight decrease in specific surface area by increasing the cobalt concentration, which is in agreement with previously reported results [32]. TGA of the samples (Figure 4-4c) showed a weight loss of ~63% between 300 and 650°C in air, which corresponds to the decomposition of ZIF into metal oxides. The observed weight loss is nearly the same as the theoretical value (64.2% for ZIF-8 and 63.6% for ZIF-67). As the amount of cobalt in ZIF increased, the thermal decomposition temperature decreased, as reported previously [32].

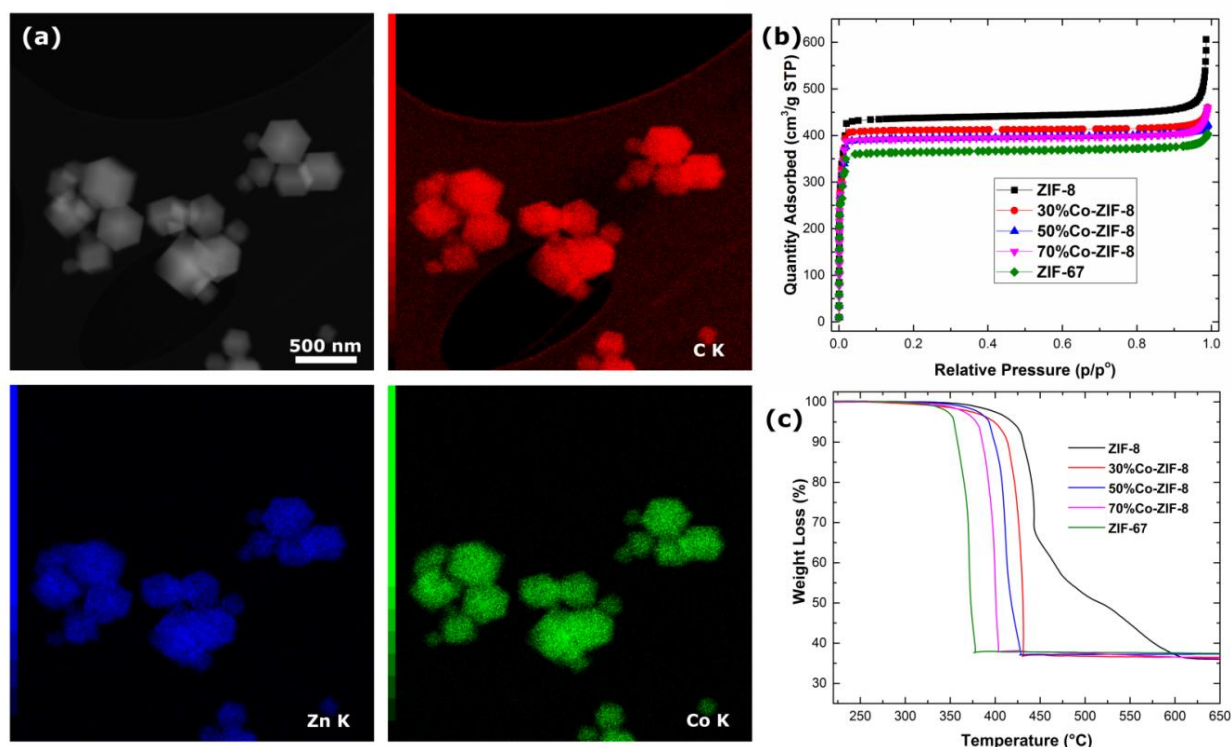


Figure 4-4 (a) STEM high-angle annular dark field image and elemental mapping images of 50%Co-doped-ZIF-8 powders, (b) nitrogen adsorption isotherm, and (c) thermogravimetric analysis of as-synthesised samples.

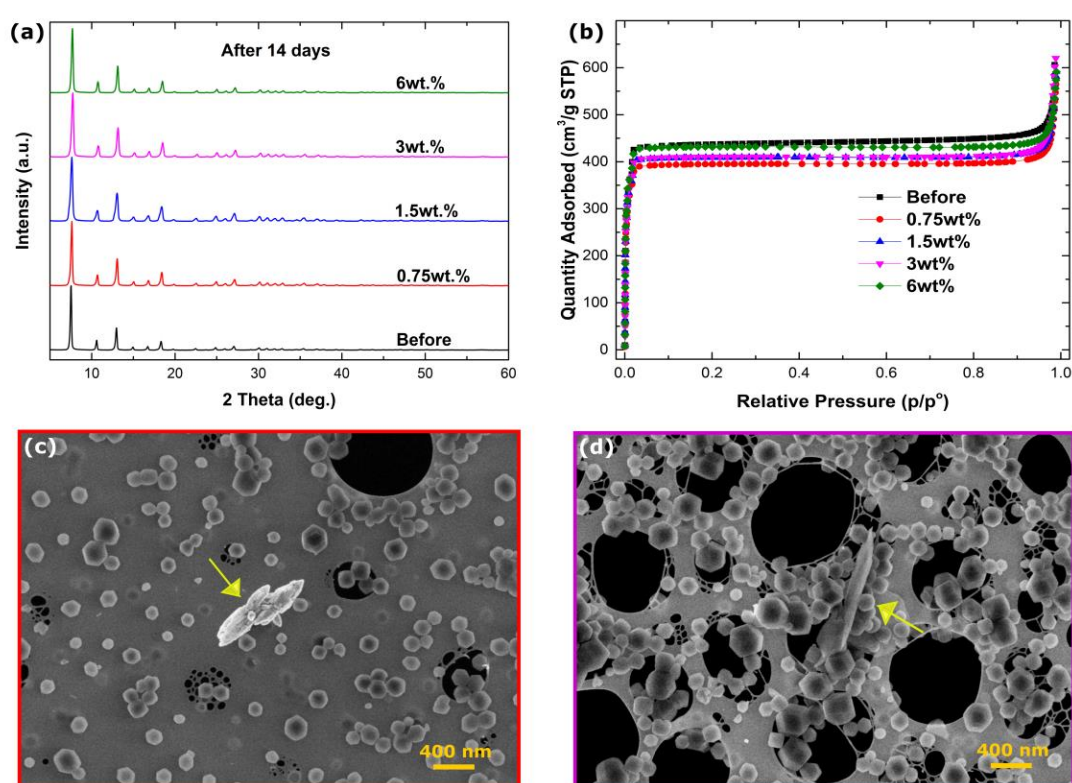
These results demonstrate that the new synthesis technique is capable of producing ZIF nanoparticles of high crystallinity with minimal amounts of ligands. In particular, it enables the production of similar particle sizes in the range of 200-400 nm regardless of cobalt doping level, which is of great importance for the study of the effect of cobalt doping on the water stability of ZIF-8.

#### 4.5.2 Effect of ZIF-8/water ratio

Figure 4-5a-b show XRD patterns and nitrogen adsorption isotherms of the filtered ZIF-8 powders after water immersion for 14 days at different powder-to-water mass ratios. As the powder-to-water mass ratio decreased from 6 to 0.75 wt%, XRD patterns did not show any change in the positions and intensity of diffraction peaks, whereas nitrogen adsorption

isotherms showed a slight reduction in adsorption. This gradual loss in porosity indicates that ZIF-8 undergoes degradation into less-porous materials.

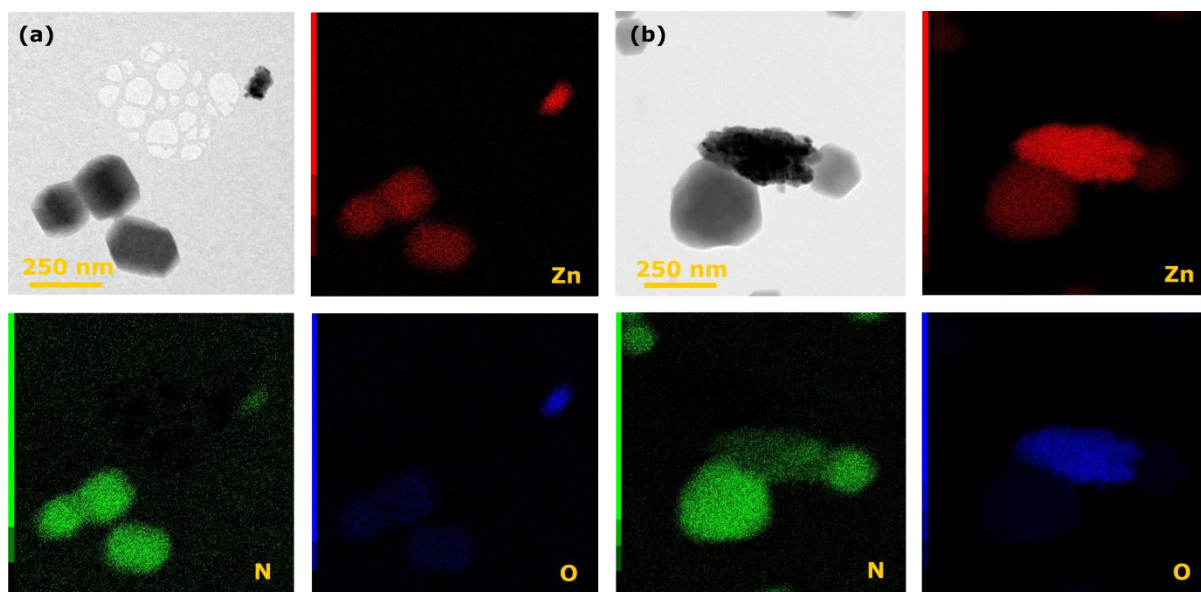
Figure 4-5c-d show SEM images of the powders after immersion for 14 days at 0.75 and 3 wt% of powder-to-water mass ratios, respectively. Although most of the particles have shapes similar to the as-synthesised sample, some particles with new morphologies (indicated with arrows) can be seen.



**Figure 4-5 (a) XRD patterns and (b) nitrogen adsorptions isotherms of the ZIF-8 samples after 14 days of immersion in DI water at different concentrations; SEM images of the filtered powders at (c) 0.75 wt% and (d) 3 wt% powder-to-water mass ratios.**

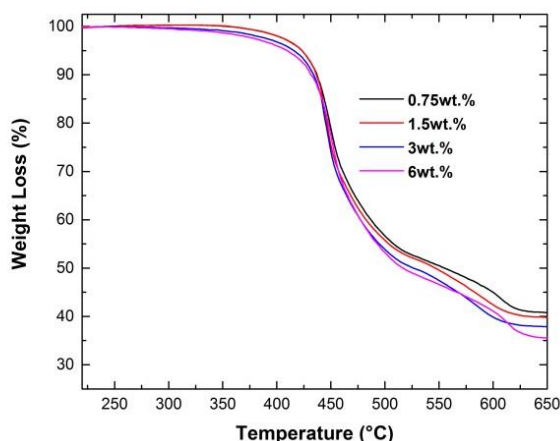
To study the elemental compositions of the unknown particles, STEM elemental mapping was conducted. The results for the filtered powders at 0.75 and 3 wt% concentrations are presented in Figure 4-6a-b, respectively. It can be seen that particles with irregular shapes are oxygen-rich and thus they can be attributed to metal oxides, hydroxides, or oxyhydroxides that are precipitated out of water.





**Figure 4-6 STEM high-angle annular dark field image and elemental mapping images of ZIF-8 samples after 14 days of immersion in DI water at (a) 0.75wt% and (b) 3wt% powder-to-water mass ratios.**

Figure 4-7 shows thermogravimetric curves of the samples after water immersion for 14 days. As the powder-to-water ratio decreased from 6 to 0.75 wt%, the weight loss decreased. The weight loss between 300 and 650°C is due to the release of gases corresponding to the decomposition of the organic ligand in ZIF-8. Hence, less weight loss means less amounts of ZIF in the filtered powder. The result indicates that, as the powder-to-water ratio decreased from 6 to 0.75 wt%, more ZIF-8 was decomposed and more oxygen-rich metal-compound precipitates were formed in the filtered powders during 14 days of immersion. This result is in good agreement with the results of nitrogen adsorptions isotherms and STEM studies in Figure 4-5 and Figure 4-6.

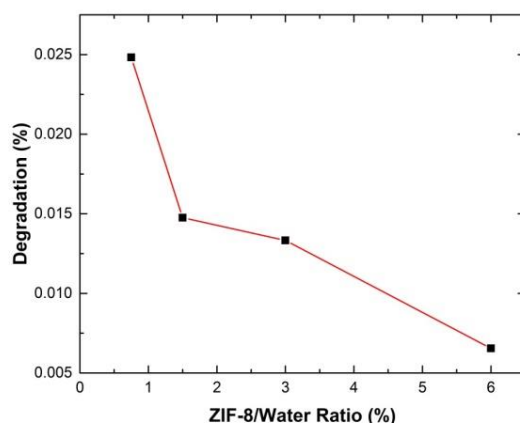


**Figure 4-7 Thermogravimetric analysis of the ZIF-8 powders after water stability test at different concentrations.**

When ZIF-8 is decomposed by hydrolysis, it releases zinc ions and Hmlm ions into water. In order to determine the amount of released zinc ions, the filtrates were analysed by Q-ICP-MS. The measured concentration of zinc ions in  $\text{mg L}^{-1}$  were correlated to the amount of degraded ZIF-8, using the following equation:

$$D = 100 \cdot \frac{C_{\text{metal}} \cdot f_{\text{dilution}}}{C_{\text{ZIF}}} \cdot \frac{M_{\text{ZIF}}}{M_{\text{metal}}} \quad (4-1),$$

where  $D$  is the degradation rate (%),  $C_{\text{metal}}$  is the concentration of metal anion in water ( $\text{mg L}^{-1}$ ),  $C_{\text{ZIF}}$  is the concentration of ZIF in water ( $\text{mg L}^{-1}$ ),  $f_{\text{dilution}}$  is the dilution factors of the filtrate used for the Q-ICP-MS analysis,  $M_{\text{ZIF}}$  is the molar mass of ZIF, and  $M_{\text{metal}}$  is the molar mass of metal anion. The result is shown in Figure 4-8. It can be seen that, in the least stable condition at a powder-to-water mass ratio of 0.75 wt%, the estimated degradation rate was only  $\sim 0.025$  wt%, which is negligible and is in disagreement with the noticeable reduction in nitrogen adsorption isotherms (Figure 4-5b) and weight loss (Figure 4-7). This low zinc concentration in the filtrate is due to the fact that most of the zinc ions were precipitated out and collected along with the ZIF powders during filtration, as confirmed by the electron microscopy study (Figure 4-5c, Figure 4-5d, and Figure 4-6).



**Figure 4-8** Calculated degradation rate (%) of ZIF-8 based on the released  $\text{Zn}^{2+}$  in filtrate at different concentrations.

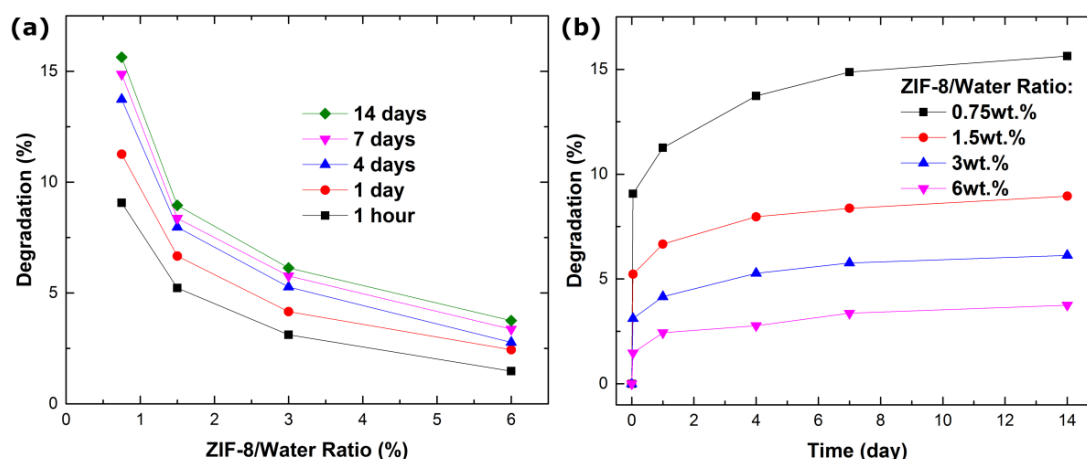
In order to determine the amount of Hmlm released from ZIF-8, the filtrates were analysed by UV-Vis spectroscopy. This was possible because Hmlm aqueous solutions have an optical absorption peak at  $\sim 200$  nm (Figure S 4-5). Using the Beer-Lambert law, the amount of Hmlm released in water can be determined with  $\text{mg L}^{-1}$  level sensitivity (Figure S 4-5). The UV-Vis absorbance spectra of the filtrates at different powder-to-water ratios and immersion durations are presented in Figure S 4-6. The measured concentration of Hmlm in  $\text{mg L}^{-1}$  is correlated to the amount of degraded ZIF-8, using the following equation:

$$D = 100 \cdot \frac{C_{\text{ligand}} \cdot f_{\text{dilution}}}{C_{\text{ZIF}}} \cdot \frac{M_{\text{ZIF}}}{M_{\text{ligand}}} \quad (4-2),$$

where  $C_{\text{ligand}}$  is the concentration of the ligand in water ( $\text{mg L}^{-1}$ ),  $C_{\text{ZIF}}$  is the concentration of ZIF in water ( $\text{mg L}^{-1}$ ),  $f_{\text{dilution}}$  is the dilution factors of the filtrate used for the UV-Vis analysis,  $M_{\text{ZIF}}$  is the molar mass of ZIF, and  $M_{\text{ligand}}$  is the molar mass of the ligand. Since the solubility of Hmlm in water is high ( $81 \text{ g L}^{-1}$  at  $25^\circ\text{C}$ ), it is assumed that no Hmlm was precipitated out during the immersion test.

Figure 4-9a shows the degradation of ZIF-8 thus estimated, as a function of powder-to-water ratio. It was found that a higher powder-to-water ratio led to less degradation of ZIF-8. When the powder-to-water ratio was increased from 0.75 wt% to 6 wt%, the degradation decreased from more than 15 wt% to less than 5 wt%.

It was proposed that the hydrolysis degradation of ZIF structures can be deemed as a reverse synthesis process and that the presence of released Hmlm can prevent further degradation [21]. It is speculated that the degradation of ZIF-8 structure becomes negligible when the concentration of the released ligand is very high.



**Figure 4-9 Degradation rate (%) of ZIF-8, calculated from the quantity of 2-methylimidazolate that is released in filtrate, as a function of (a) powder-to-water ratio and (b) immersion time**

Figure 4-9b shows the degradation of ZIF-8 as a function of immersion time. Most of the degradation occurred in the first hour of immersion in water and then slowed down over time. The initial dissolution in the first hour can be interpreted as a non-equilibrium regime in the dissolution process [41]. Degradation rates of ZIF-8 nanoparticles at different powder-to-water ratios were analysed using a modified first-order reaction rate kinetic equation that is frequently applied to the dissolution of nanoparticles, following the reaction-diffusion kinetic model proposed by David *et al.* [41,42]. The results of curve fitting and degradation rate constants are shown in Figure S 4-7. The rate constant at a powder-to-water ratio of 6 wt% was nearly half of that at a powder-to-water ratio of 1.5 wt%. The degradation rate constant at a powder-to-water ratio of 0.75 wt% was slightly lower than that at a powder-to-water ratio of 1.5 wt%, due possibly to its high initial degradation (~9 wt%) in the first hour [43]. Equilibrium degradation values, which represent the final equilibrium concentration of dissolved ZIF-8 at  $t = \infty$ , at a powder-to-water ratio of 6 wt% was nearly three times less than that at a powder-to-water ratio of 0.75 wt%.

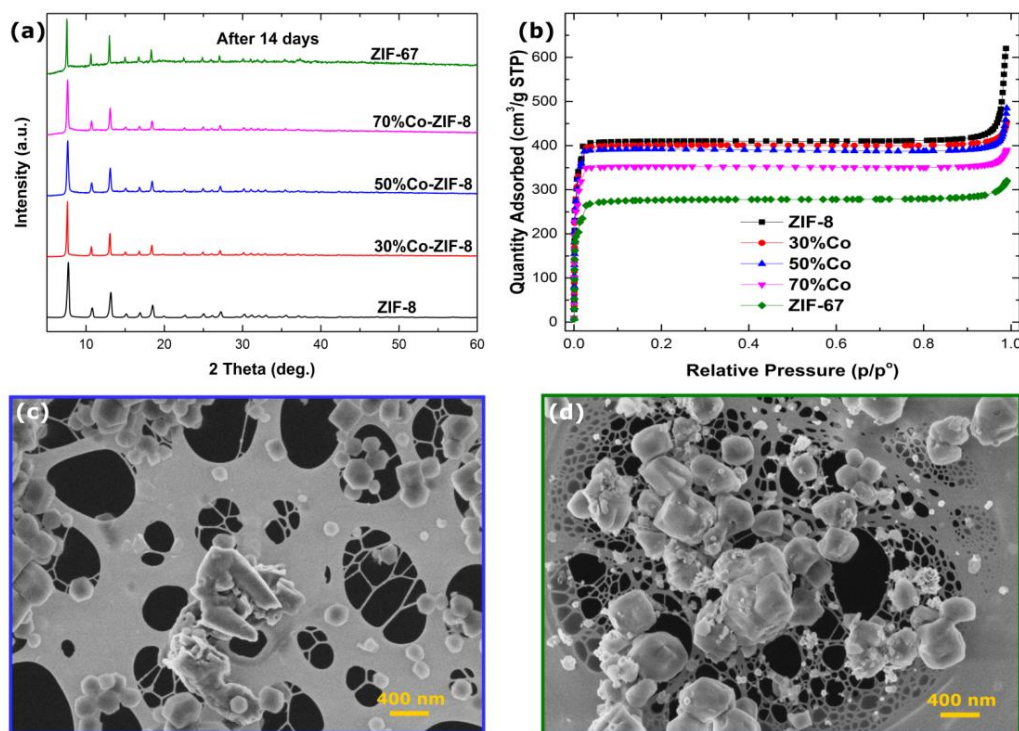
It is noteworthy to mention that the ligands used in other MOFs, such as benzene-1,4-dicarboxylic acid ( $H_2BDC$ ) and benzene-1,3,5-tricarboxylic acid ( $H_3BTC$ ), can be detected at very low concentrations in water by UV-Vis spectroscopy (Figure S 4-8). Hence it is believed that UV-Vis spectroscopy can be used to quantitatively study the water stability of a wide range of MOF materials.

#### 4.5.3 Effect of cobalt doping level on ZIF-8 stability

The effect of cobalt doping level on the water stability of ZIF-8 was investigated using the same combination of analytical tools, on both filtered powders and the filtrate liquid.

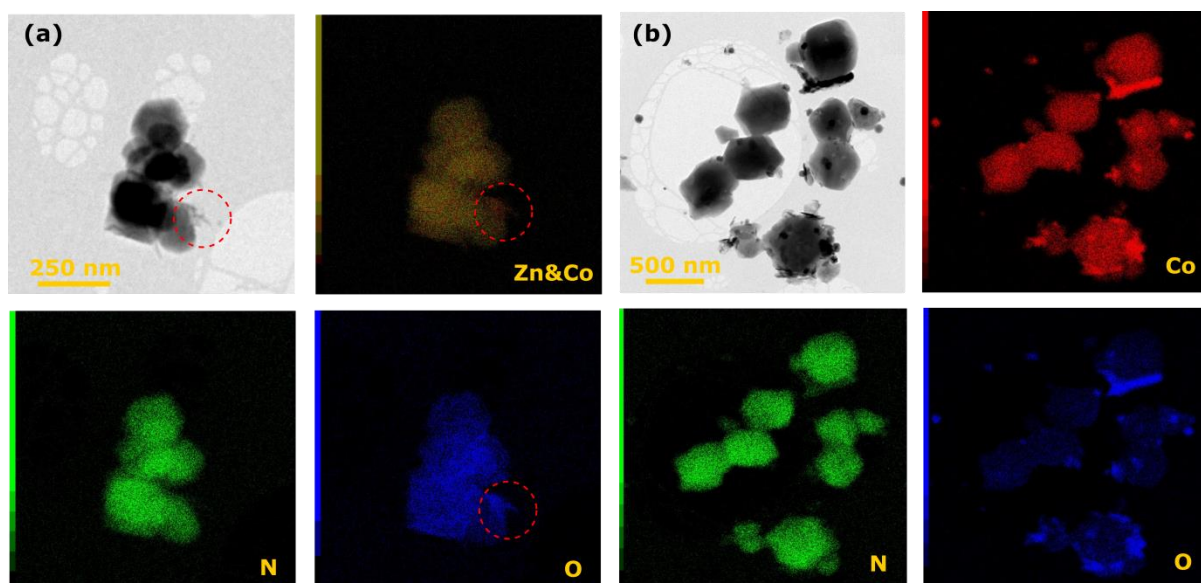
The XRD patterns of the filtered powders after 14 days of immersion are presented in Figure 4-10a. For the samples ZIF-8, 30%Co-ZIF-8, 50%Co-ZIF-8, and 70%Co-ZIF-8, the diffraction peaks did not show any change in their intensity and position. However, the XRD pattern of ZIF-67 showed a higher background and one extra peak at  $37.4^\circ$ , compared to the XRD pattern before immersion. Nitrogen adsorption isotherms of the samples after 14 days of immersion (Figure 4-10b) showed a clear decreasing trend in specific surface area by increasing the amount of cobalt in the ZIF structure. The results of XRD and nitrogen adsorption isotherms suggest that Co-N bonds are more susceptible to hydrolysis than Zn-N bonds in the ZIF structure [44].

SEM images of 50%Co-ZIF-8 and ZIF-67 powders after 14 days of immersion are presented in Figure 4-10c-d, respectively. The images unveil the precipitation of a considerable amount of irregularly shaped particles in the filtered powders. High-resolution SEM images of filtered ZIF-67 powders (Figure 4-10d) reveals the formation of  $\sim 30$  nm size precipitates.



**Figure 4-10 (a) XRD patterns and (b) nitrogen adsorptions isotherms of the cobalt-doped-ZIF-8 samples after 14 days of immersion in DI water at 3 wt% concentration; SEM images of (c) 50%Co-ZIF-8 and (d) ZIF-67 powders.**

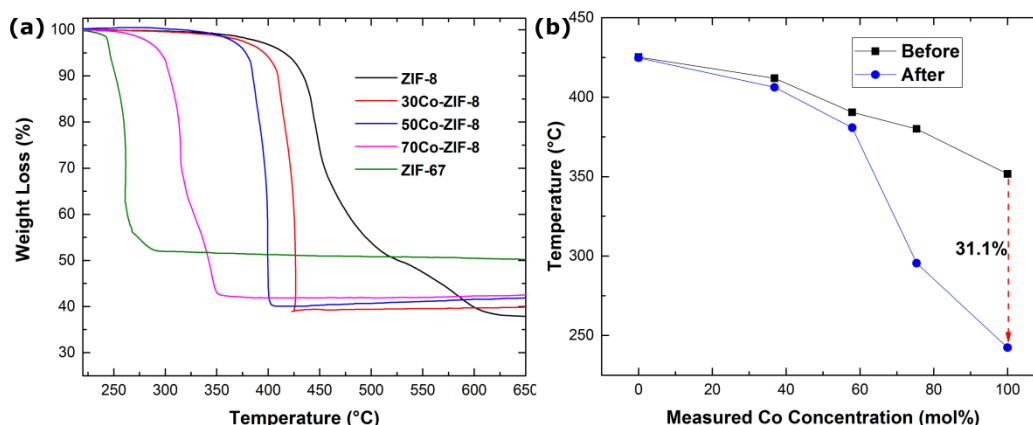
Figure 4-11 shows a STEM HAADF image and elemental mapping images of 50%Co-ZIF-8 and ZIF-67 powders after 14 days of water immersion. These images endorse that oxygen-rich particles with irregular shapes precipitated out during the stability test, which resulted in the lower specific surface area of the collected powder samples (Figure 4-10b).



**Figure 4-11** STEM high-angle annular dark field image and elemental mapping images of (a) 50%Co-ZIF-8 and (b) ZIF-67 powders, after 14 days of immersion in DI water at 3 wt% powder-to-water mass ratio.

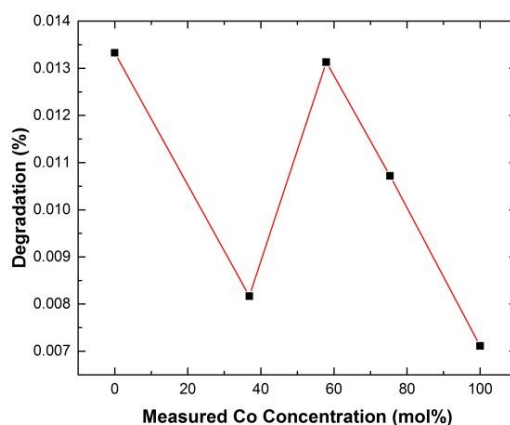
The thermogravimetric analysis of the filtered powders (Figure 4-12a) after 14 days of water immersion shows that, not only weight loss but also thermal stability decreased by increasing the cobalt content in ZIF-8. The decrease in weight loss confirms that the filtered powders contained precipitates that do not contribute to the weight loss. It also indicates that a higher cobalt content results in higher susceptibility to hydrolysis. Figure 4-12b shows the comparison of the onset temperatures of the thermal decomposition before and after water immersion. The data reveal that the thermal stability of ZIF particles decreased drastically when the cobalt-doping level was increased over 50 at%.





**Figure 4-12 (a) Thermogravimetric curves of cobalt-doped ZIF-8 powders after water immersion for 14 days; (b) Thermal-decomposition onset temperature of doped ZIF-8 before and after water-immersion.**

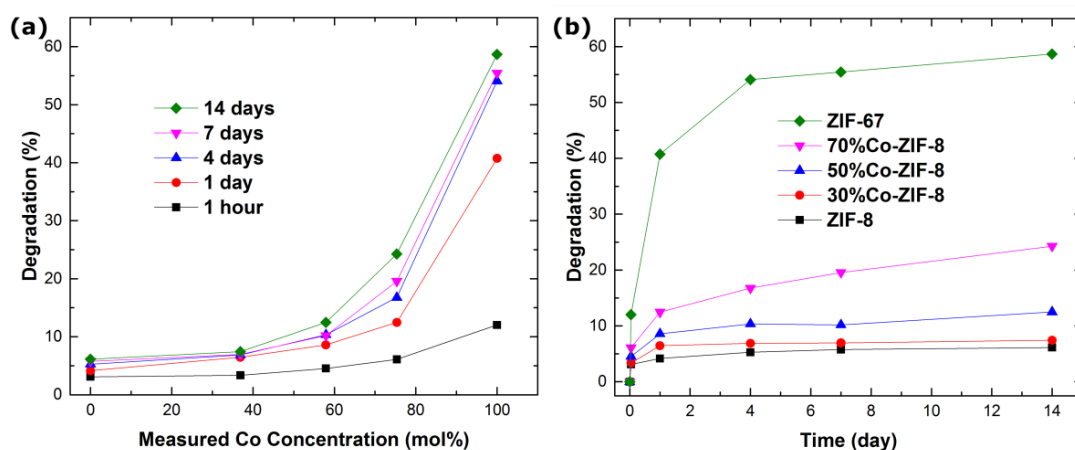
In order to determine the amount of released zinc and cobalt ions, the filtrates were analysed by Q-ICP-MS. The measured concentration of metal ions in  $\text{mg L}^{-1}$  was correlated to the amount of degraded ZIF-8, using Equation (4-1). As shown in Figure 4-13, the detected amounts of metal ions corresponded to only less than 0.014% degradation, for the whole cobalt concentration range. Moreover, there was no clear trend in the corresponding degradation rate as a function of cobalt concentration. This is because most of the metal ions were precipitated out in the form of nanoparticles as shown in Figure 4-10 and Figure 4-11. Hence, ICP-MS of filtrates is not a useful tool to analyse the water stability of cobalt-doped ZIF-8.



**Figure 4-13 Calculated degradation value (%) of cobalt-doped-ZIF-8 powders based on the released  $\text{Zn}^{2+}/\text{Co}^{2+}$  in the filtrate.**



However, UV-Vis spectroscopy of the filtrates showed a clear trend over the studied immersion time. The UV-Vis absorbance value of the diluted filtrate of cobalt-doped-ZIF-8 aqueous suspensions at 200 nm (Figure S 4-9) was converted to the degradation rate using Equation (4-2). As shown in Figure 4-14, the degradation rate was lower at lower cobalt doping levels. This is in agreement with the XRD, BET, and TGA results (Figure 4-10 and Figure 4-12). Notably, the instability of cobalt-doped-ZIF-8 accelerated significantly after 50 at% doping, in good agreement with the result of the TGA study (Figure 4-12b). After about 4 days of immersion in DI water, the dissolution of ZIFs reached a near-saturation level (Figure 4-14b). After 14 days, the degradation reached 24.3 and 58.7 % for 70%Co-ZIF-8 and ZIF-67, respectively. It was not possible to calculate the degradation rate constant of cobalt-doped ZIF samples by applying the reaction rate kinetic equation that was used for Figure 4-9, because the equation is not valid when the particle size changes drastically during the dissolution due to extensive particle degradation [41] which was the case for 70%Co-ZIF-8 and ZIF-67.



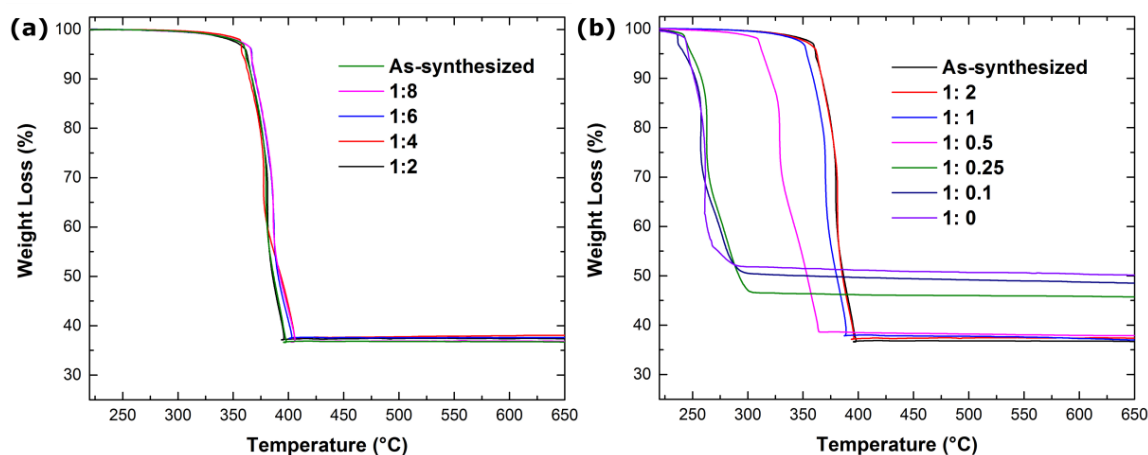
**Figure 4-14** Degradation rate (%) of cobalt-doped-ZIF-8 powders, calculated from the released 2-methylimidazolate in filtrate, as a function of (a) cobalt concentration and (b) immersion time.

In order to confirm that it is in fact necessary to use particles of similar sizes for studying the effect of cobalt doping on the stability of ZIF powders, the effect of particle size on the degradation rate of ZIF-67 was investigated. It was found that, in agreement with the Velásquez-Hernández's report [26], smaller particle sizes resulted in faster degradation;

after one day of immersion, ZIF-67 particles of 200-400 nm in diameter degraded almost twice as much as ZIF-67 particles of  $> 1\ \mu\text{m}$  in diameter (Figure S 4-10). This highlights the importance of the new mechanochemical synthesis route that allows the formation of similar sizes of ZIF powders irrespective of cobalt-doping levels.

#### 4.5.4 Effect of extra HmIm

It is speculated that adding an extra amount of ligands in water can prevent the hydrolysis of ZIF structures [20,21]. In order to find the minimum amount of HmIm required to stabilise ZIF-67, TGA was carried out for the samples immersed in water for 14 days at a powder-to-water mass ratio of 3 wt%. Figure 4-15 shows the TGA curves of the ZIF-67 powders after water immersion at different ZIF-67-to-extra-ligand molar ratios (from 1:0 to 1:8). When the ratio was higher than 1:2, there was a negligible difference between before and after the immersion test, in the weight loss and the onset temperature of thermal decomposition (Figure 4-15). However, reducing the ratio below 1:2 resulted in lower onset temperatures of thermal decomposition and less weight losses (Figure 4-15b), suggesting the loss of water stability. The results indicate that it is possible to stabilise ZIF-67 in water by adding HmIm and that TGA can be used to determine the amount of HmIm required to stabilise the ZIF structure in water.



**Figure 4-15** Thermogravimetric analysis of the ZIF-67 powders after water stability test in presence of extra ligand at different molar ratio of ZIF-67 to ligand (from 1:0 to 1:8).

The degradation of ZIF-67 after 4 days was insignificant. After 4 days of water immersion, 54.1 wt% of ZIF-67 degraded, where the molar ratio between the non-degraded ZIF-67 (45.9 wt%) and the released Hmlm (39.6 wt%) is equal to 1:2.3. This means that the degradation of ZIF-67 is negligible when the molar ratio of ZIF-67-to-extra-ligand is more than 1:2.3. This ratio is in a reasonable agreement with the results of TGA analysis (Figure 4-15) where the amount of Hmlm required to stabilise 3 wt% ZIF-67 was approximately 1:2 (Figure 4-15).

## 4.6 Conclusions

In this study, the water stability of ZIF-8 and cobalt-doped ZIF-8 was studied by combining many analytical techniques. In the past, water stability of MOFs was investigated mainly using powder XRD, surface area analysis, electron microscopy of filtered powders, and ICP-OES or ICP-MS analysis of filtrates. This chapter showed that these analytical techniques are not sufficiently sensitive to quantitatively detect the hydrolysis degradation of ZIF structures. It was demonstrated for the first time that, among the studied analytical techniques, UV-Vis spectroscopy is the most sensitive method to detect the hydrolysis of ZIF structures. This method can be used to quantitatively study the water stability of a wide range of MOF materials, as many common ligands in MOF structures can be detected in water by UV-Vis spectroscopy with high sensitivity. This chapter also showed for the first time that TGA analysis is effective in detecting the presence of metal-compound precipitates in the immersed ZIF powders and also in determining the minimum amount of additional ligands in water required to stabilise ZIF structures.

In addition, the study demonstrated a new synthesis method of cobalt-doped ZIF-8 nanopowders. Unlike direct aqueous precipitation methods, a mechanochemical ball milling method allowed the production of highly crystalline ZIF nanoparticles with similar sizes in the range of 200 – 400 nm, independent of cobalt-doping levels. This enabled the study of the effect of cobalt doping level on the water stability of ZIF-8, while avoiding the effect of

particle size on water stability. Of particular importance is the ability of this method to produce ZIFs with minimal waste of ligands; the metal-acetate-to-HmIm molar ratio of only 1:8 was necessary to produce single-phase SOD-ZIF-8 powders. It is also interesting to note that the mechanochemical reaction induced the formation of  $\text{Zn/Co(HmIm)}_2$  between zinc acetate and HmIm, which may be of interest to the synthesis of a variety of metal organic compounds without using organic solvents.

Through this study, a new understanding of the effects of ZIF concentrations in water, cobalt doping levels, and amounts of extra ligands in water, on the water-stability of ZIFs was obtained. It was found that, the water stability of ZIF decreases as the concentration of ZIFs in water decreases. Most of the degradation occurs in the first hour of immersion in water and then slows down over time. After 14 days of immersion in water, about 15% of ZIF-8 was degraded at a ZIF concentration of 0.75 wt%. It was also found that the water stability of ZIF-8 decreases as the cobalt-doping level increases. After 14 days of immersion in water, nearly 60% of ZIF-67 (i.e., 100% cobalt-doping) degraded at a concentration of 3 wt%. The TGA results indicated that it is possible to stabilise ZIF-67 in water by adding ligands in water. The minimum amount of HmIm required to stabilise ZIF-67 in water at 3 wt% ZIF-concentration was 2 molar HmIm to 1 molar ZIF-67.

The findings have significant implications for the study of MOFs in water-based applications. For example, the results of the catalytic and photocatalytic applications of MOFs in water should be carefully analysed, depending on the extent of MOF's hydrolysis. The effects of metal oxide precipitates such as ZnO (photocatalyst) or  $\text{Co}_3\text{O}_4$  (redox catalyst) should be considered in the interpretation of the data. The results of heavy-metal scavenging by MOFs in water should also be affected by the hydrolysis of MOFs; heavy metals may be separated from water by the formation of precipitates of heavy-metal-compounds, not by catalytic or photocatalytic redox reaction by MOFs, but by reaction with metal ions or ligands released from MOFs [45–47]. The proposed combination of analytical tools to quantitatively study the

water stability of MOFs will enable the researchers to make better selections of MOFs for water-related applications and more accurate interpretations of their results than previously possible.

## 4.7 References

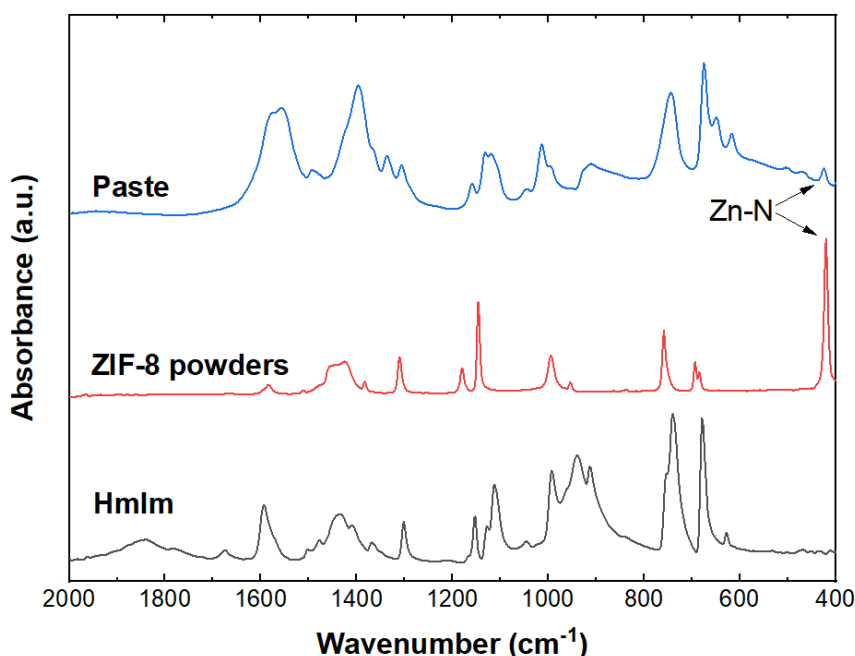
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## 4.8 Supplementary Information



**Figure S 4-1** FTIR spectra of the viscous paste resulted from ball milling of zinc acetate and 2-methylimidazole (molar ratio of 1 to 8) in comparison with ZIF-8 powders and 2-methylimidazole reagent



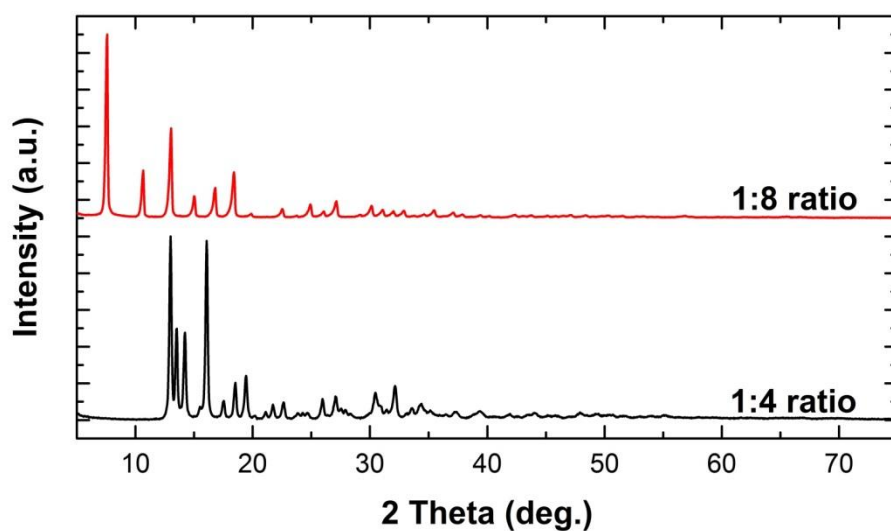


Figure S 4-2 XRD patterns of the samples milled at zinc acetate to 2-methylimidazole ratios of 1 to 4 (bottom) and 1 to 8 (top)

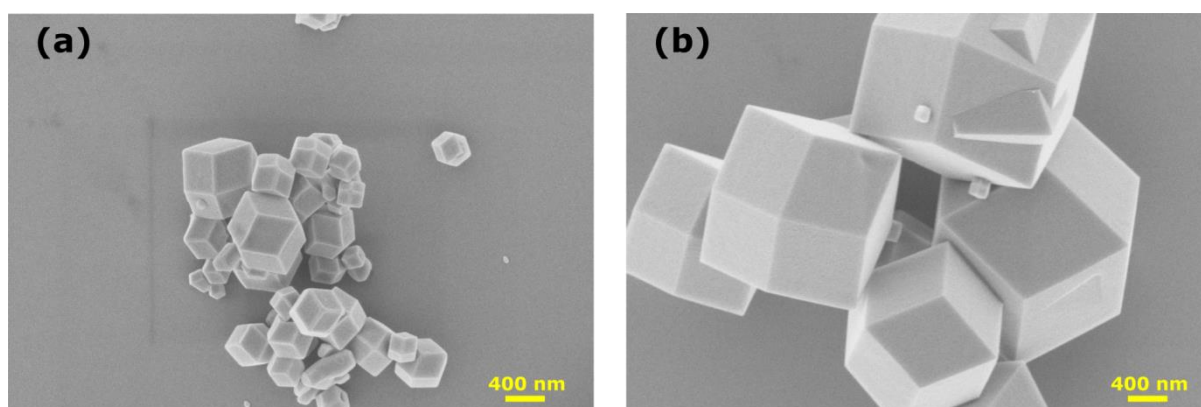


Figure S 4-3 SEM images of (a) ZIF-8 and (b) ZIF-67 synthesised by mixing aqueous solutions of zinc acetate and 2-methylimidazole at a molar ratio of 1 to 8

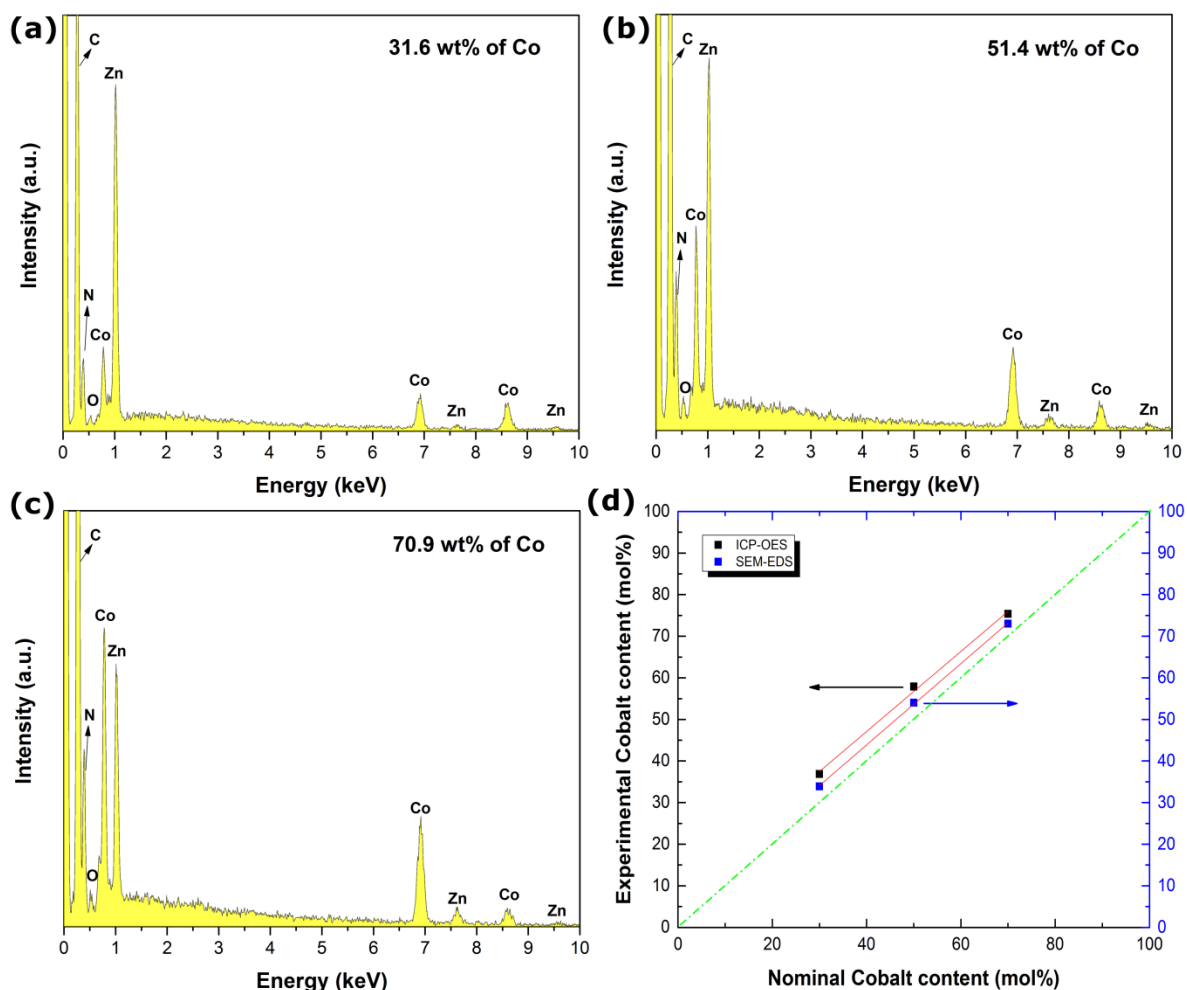


Figure S 4-4 Energy dispersive X-ray spectroscopy of (a) 30%Co-ZIF-8, (b) 50%Co-ZIF-8, (c) and 70%Co-ZIF-8; (d) experimental cobalt contents (mol%) measured by ICP-OES and energy-dispersive X-ray spectroscopy (SEM-EDS) in Co-doped-ZIF-8 powders, with respect to their nominal cobalt content (mol%).

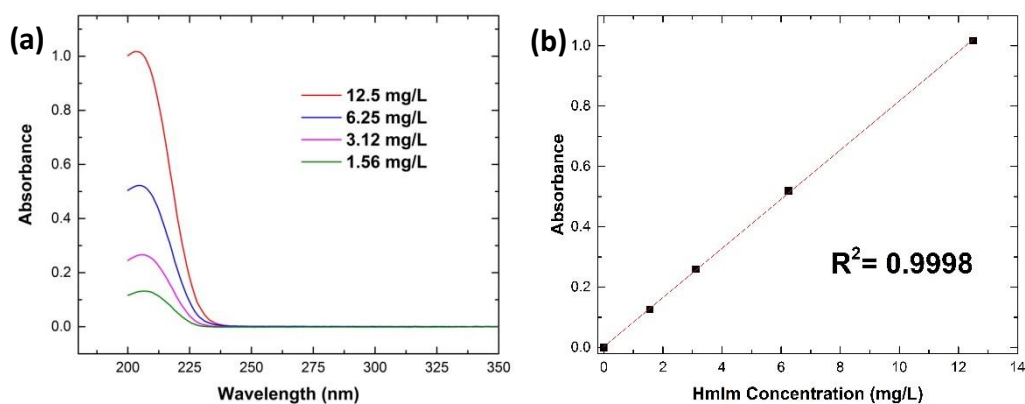


Figure S 4-5 (a) UV-Vis spectra of dissolved 2-methylimidazole in DI water at different concentrations; (b) a calibration line for determining the concentration of the ligand in water

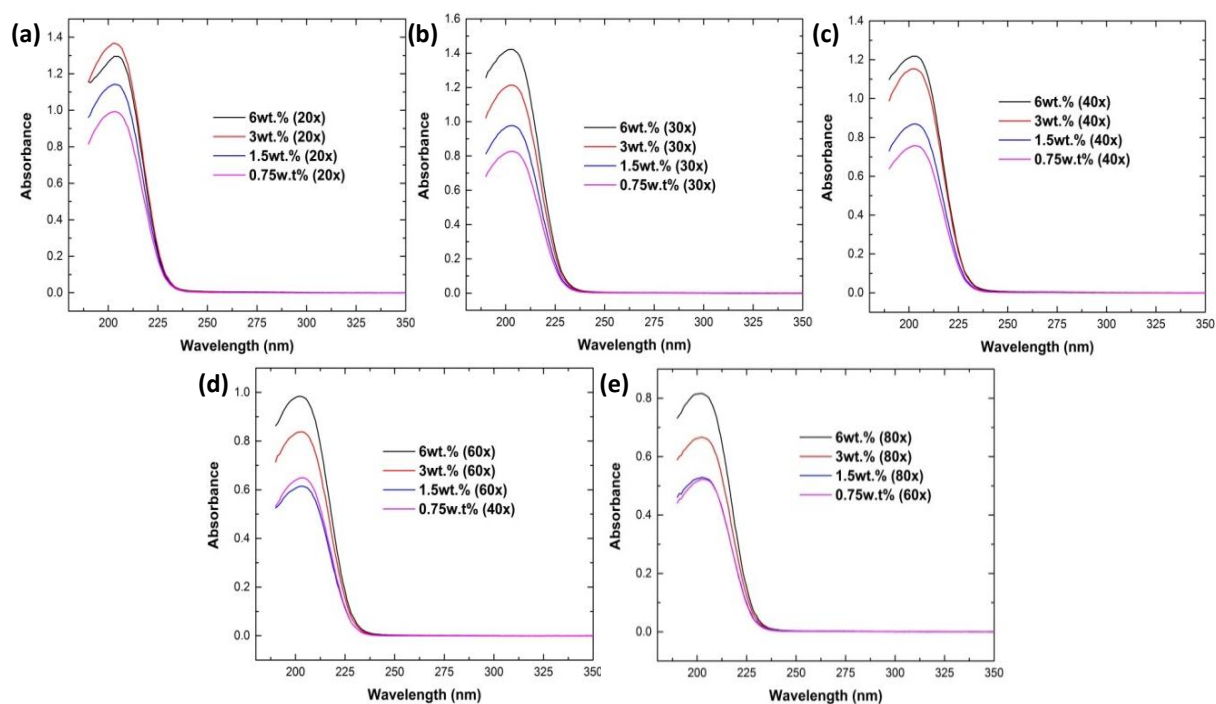
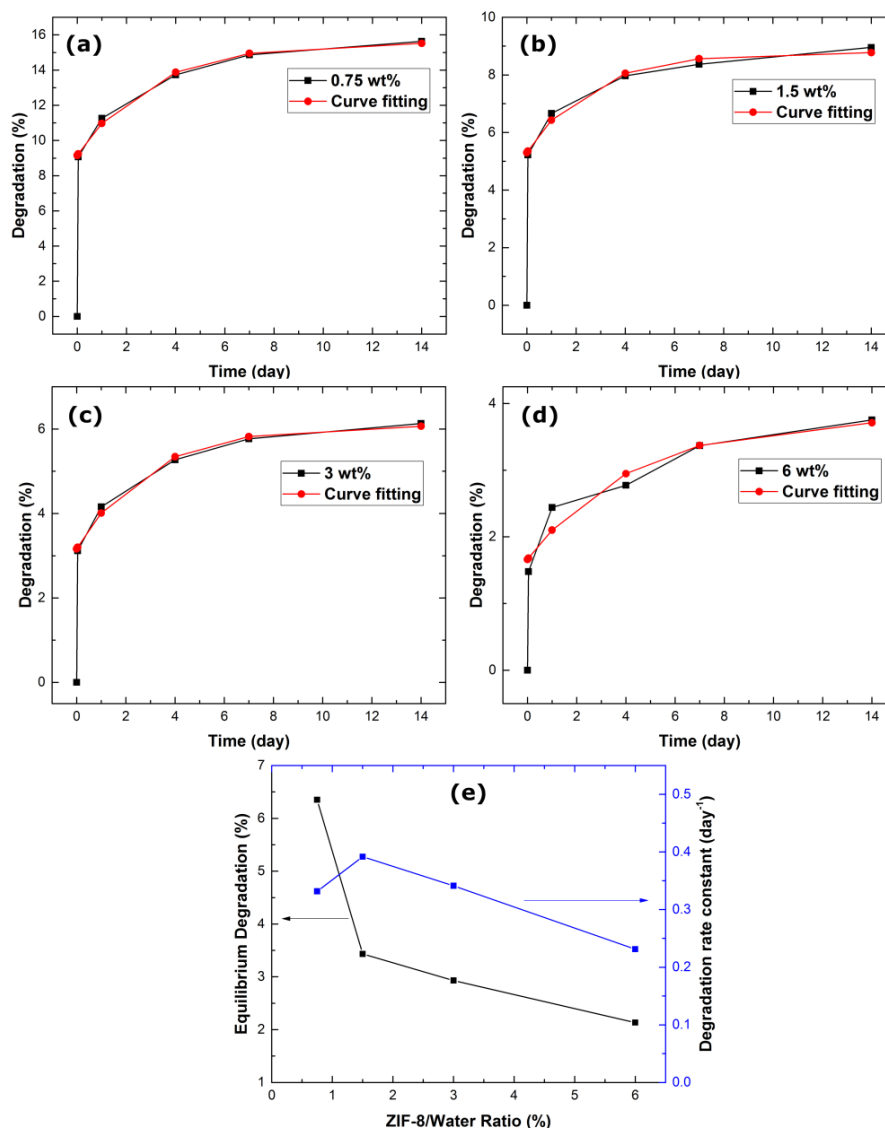


Figure S 4-6 UV-Vis spectra of the diluted filtrate of ZIF-8 aqueous suspension at different ZIF/water ratios, after (a) 1 hour, (b) 1 day, (c) 4 days, (d) 7 days, and (e) 14 days of immersion



**Figure S 4-7** Degradation rate (%) of ZIF-8, as a function of immersion time at powder-to-water ratios of (a) 0.75, (b) 1.5, (c) 3, and (d) 6 wt%. The red line denotes the results of curve fitting using the modified kinetic equation. (e) Equilibrium degradation (%) and Degradation rate constant ( $\text{min}^{-1}$ ) as a function of powder-to-water ratio (%)

**Note:** The modified kinetic equation [4-S1] is:

$$y(t) = y_0 + (y_f - y_0) \times (1 - e^{-kt}) \quad (4-S1),$$

where  $y(t)$  is the degradation of ZIF-8 at time  $t$  (day),  $y_0$  is the initial value of degradation,  $y_f$  is the final value of degradation, and  $k$  is the degradation rate constant ( $\text{day}^{-1}$ ). The equilibrium degradation can be described as  $(y_f - y_0)$ . The curve fitting was conducted for the data points above 1 hour of immersion time.

**Reference [S1]** C.Y. Leung, Y. Tu, B.Z. Tang, W.-X. Wang, Dissolution kinetics of zinc oxide nanoparticles: real-time monitoring using a  $\text{Zn}^{2+}$ -specific fluorescent probe, *Environ. Sci. Nano.* 6 (2019) 2259–2268. doi:10.1039/C9EN00553F.

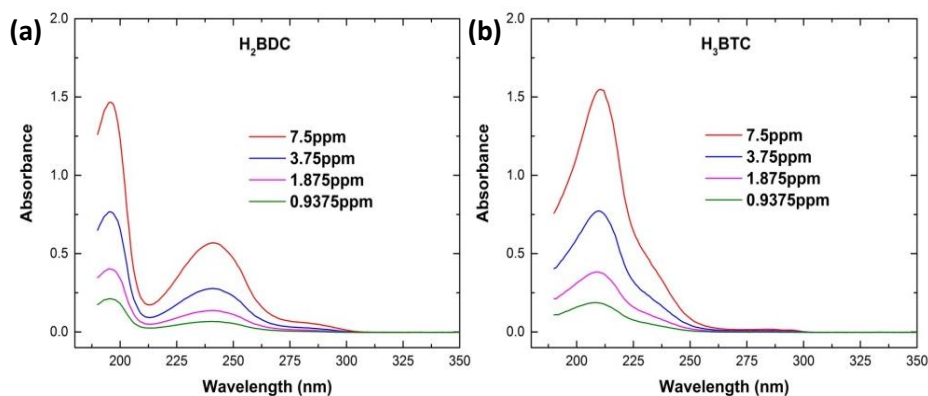


Figure S 4-8 UV-Vis spectra of dissolved (a) benzene-1,4-dicarboxylic acid ( $\text{H}_2\text{BDC}$ ) and (b) benzene-1,3,5-tricarboxylic acid ( $\text{H}_3\text{BTC}$ ) in water at different concentrations

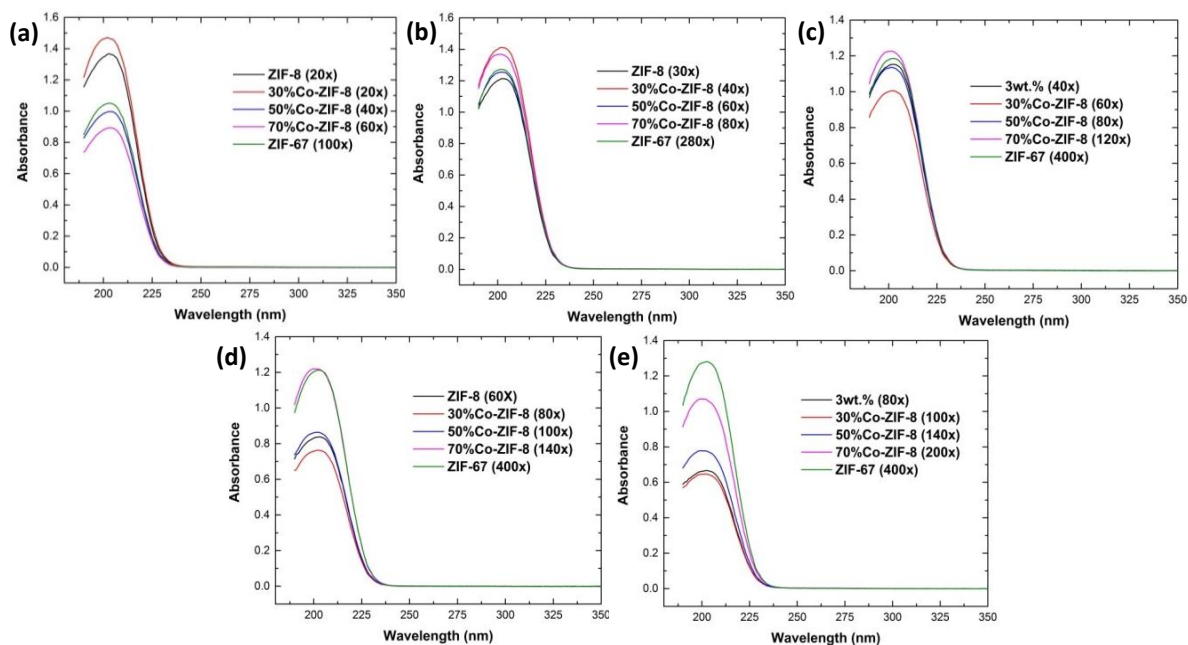
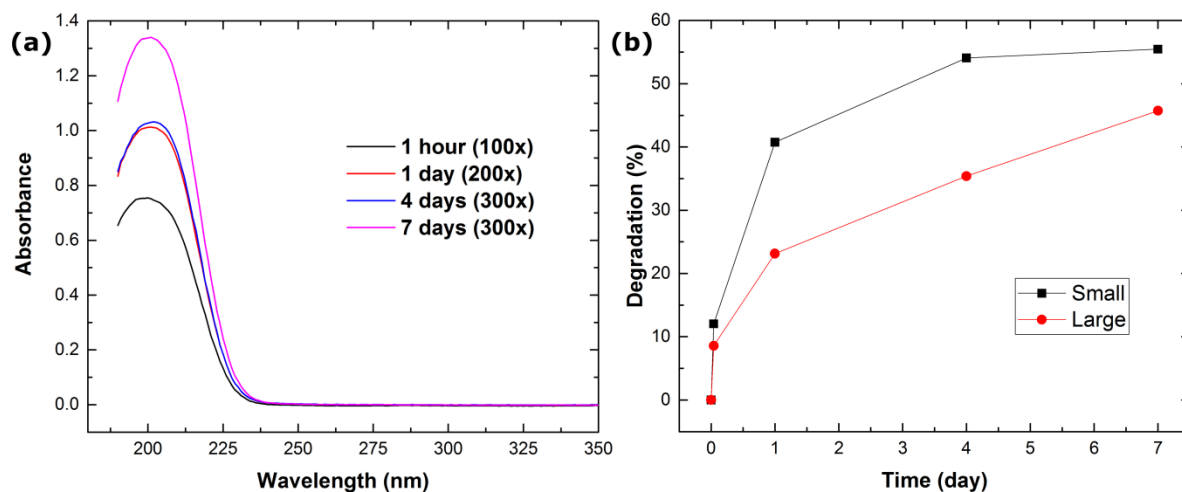


Figure S 4-9 UV-Vis spectra of the diluted filtrate of cobalt-doped-ZIF-8 aqueous suspensions at different cobalt-doping levels after (a) 1 hour, (b) 1 day, (c) 4 days, (d) 7 days, and (e) 14 days of immersion



**Figure S 4-10 (a)** UV-Vis absorbance spectra of the diluted filtrate of aqueous suspensions of large ZIF-67 after different immersion times, and **(b)** degradation rates of ZIF-67 powders as a function of immersion time. ZIF-67 powders of 200-400 nm and  $>1\ \mu\text{m}$  in diameter are denoted as small and large, respectively. The degradation rate was calculated based on the amount of released 2-methylimidazolate in the filtrate in Figure S 4-9 and Figure S 4-10a

**Note:** ZIF-67 particles of  $>1\ \mu\text{m}$  in diameter (see Figure S 4-3b) were synthesised by mixing aqueous solutions of zinc acetate and 2-methylimidazole with a molar ratio of 1 to 8.

## Chapter Five (Part I)

### Stability of ZIF-8 nanopowders in bacterial culture media and its implication for antibacterial properties

#### 5.1 Preamble

The publication relevant to this chapter is “M. Taheri\* & D. Ashok\*, T. Sen, T. G. Enge, N. K. Verma, A. Tricoli, A. Lowe, D. Nisbet, T. Tsuzuki, Stability of ZIF-8 nanopowders in bacterial culture media and its implication for antibacterial properties, Chemical Engineering Journal, In press, pp 127511.” The relevant supporting information is presented in Section 5.8. The antibacterial property of ZIF-8 was carried out in collaboration with Mr. Deepu Ashok in Prof. David Nisbet’s group at the Australian National University.

#### 5.2 Abstract

The stability and degradation characteristics of metal organic frameworks (MOFs) in liquid media dictate their use in biomedical engineering applications. In this study, the antibacterial property of a zinc-based MOF, zeolite imidazolate framework-8 (ZIF-8), against gram-negative *Escherichia coli* (*E. coli*) is studied in comparison with ZnO, a widely-used antimicrobial agent. Superior antibacterial properties of ZIF-8 were demonstrated, and the reasons were elucidated by new insights on the stability of ZIF-8 in bacterial culture media. Contrary to the widely held notion that ZIF-8 is stable in aqueous media, inductively coupled plasma-optical emission spectrometry and UV-Vis absorption spectroscopy revealed the release of zinc ions and 2-methylimidazolate molecules in the culture media. Electron microscopy and X-ray diffractometry revealed that the degradation of ZIF-8 is enhanced by the reaction of released zinc ions with phosphate ions in phosphate-buffered saline (PBS) or with organic moieties in Luria Bertani (LB) media, resulting in stronger antibacterial properties of ZIF-8 than that of ZnO. In fact, due to the affinity of ions and organic constituents in the cell media towards the building block of ZIF-8, a higher amount of ZIF-8

degrades in LB and PBS media (70-80 wt%) than in pure water (22 wt%) after 24 hours of immersion. The results of this chapter strongly advocate the importance of stability study on MOFs in developing their biomedical applications, in terms of their efficacy, biosafety, and eco-safety.

### 5.3 Introduction

Recently, metal organic frameworks (MOFs) have attracted significant attention in biomedical research [1–3]. A prominent example is zeolite imidazolate frameworks-8 (ZIF-8), a MOF that resembles zeolites in topology [4]. Like zeolites, ZIF-8 contains regularly shaped pores and channels that only permit the migration of certain molecules [5,6]. The hybrid framework of ZIF-8 offers more flexibility in surface modification and often allows rational tuning of surface properties compared to zeolites, along with better thermal, hydrothermal and chemical properties compared to other MOFs [4,5,7–9]. As such, ZIF-8 nanoparticles have found their way in many biomedical applications that include tissue engineering [10,11], drug delivery [12–15], and antimicrobial therapy [16–18].

ZIF-8 has also been extensively investigated for other aqueous applications including desalination [19], biocatalysis/catalysis [20,21], and oil/water separation [22]. This is because it has long been thought that ZIF-8 is thermodynamically stable in water [23]. However, recent studies proved otherwise [24–26]. For instance, when ZIF-8 was subjected to deionised (DI) water, its structure was disrupted whereby it hydrolysed into zinc and imidazolate ions or transformed into partially hydrolysed ZIF-8 structures [25]. In the previous chapter, it was quantitatively shown that ZIF-8's stability is inversely proportional to the concentration of ZIF-8 and that most of the degradation occurs in the initial hours of immersion [24, Chapter 4]. These findings have been further extended to study the effect of heat treatment on the water stability of  $\text{NH}_2\text{-MIL-125(Ti)}$  using quantitative analysis of the released ligand in the filtrate [27].



The recent findings on the degradation behaviour of ZIF-8 have significant implications for their utility. Thus, for the development of MOFs' applications, it is critical to understand their degradation characteristics in different liquid media, especially for energy [28–30] and biomedical [31–33] applications.

The nature and products of degradation are governed by the physicochemical properties of the liquid media, with the degradation products also impacting the chemical environment in the liquid media [34–36]. However, degradation characteristics in different liquid media have been largely overlooked to date [14,17,37–41], with only a few studies investigating the stability of ZIF-8 in different cell-culture media [42–44]. Velasquez-Hernandes *et al.* investigated the degradation of ZIF-8 in a 10 mM phosphate-buffered saline solution [42]. Their study showed a rapid decomposition of ZIF-8 frameworks resulting in the formation of insoluble zinc phosphate particles. The decomposition rate was found to be inversely proportional to the size of the ZIF-8 particles [42]. When ZIF-8 is immersed in buffer solutions containing carbonates and phosphates, the morphology and chemistry of ZIF-8 particles were altered but cargo release from ZIF-8 was not induced [44]. In contrast, immersion in serums and cell-media induced morphological changes to ZIF-8 and also caused cargo release from ZIF-8 [44]. Since the degradation characteristics of ZIF-8 in liquid media not only depend on the chemistry of the liquid media but also on the concentration of ZIF-8 in the media that is specific to each application, it is important to carefully assess the degradation characteristics of ZIF-8 under each application condition.

Antimicrobial applications of ZIF-8 and ZIF-8-based composites have significant potential [45–57], due to their inherent highly porous structure [16,37,58–62], coupled with their ability to act as a reservoir of metal ions (zinc ions in case of ZIF-8). Zinc ions are a potent antimicrobial agent as it can induce cell deformation, rupture of the cell wall causing leakage of the cytoplasm, creation of an alkaline microenvironment, all of which lead to the growth inhibition or death of the bacterium [63,64]. This means that they can be engineered to

control their ion-release, which is an attractive property for many biomedical applications [65,66]. Antibacterial properties of ZIF-8 have found their way in many applications such as implant coatings [37], water filtration [45], and multifunctional fabrics [67]. Therefore, it is essential to understand the chemistry of ZIF-8 particles and the ion release kinetics in culture media. In fact, previous reports on the influence of bacterial media on the antibacterial effects of nanoparticles of ZnO and silver (Ag) showed their variable cytotoxicity influenced by the interaction between the nanoparticles and the constituents of the media [34,35]. Since there are no similar studies for ZIF-8, it is essential to understand how the exposure environment dictates the release of zinc ions and the resulting cytotoxicity towards bacteria.

The research gap has led us to study the relationship between the antibacterial property of ZIF-8 and its stability in different bacterial culture media. ZnO nanoparticles were used as a benchmark to compare the antibacterial property against Ampicillin-resistant *Escherichia coli* (*E. coli*). To achieve this, the release of zinc ions from ZIF-8 particles was compared to that from ZnO in two popular bacterial media, namely Luria Bertani (LB) and phosphate-buffered saline (PBS) solution. The toxicity analysis in DI water was not performed, because normal physiological functions of bacteria will be damaged in DI water due to the release of solutes from the cells in response to the osmotic down-shock [35]. In this chapter, it is elucidated how the exposure environment affects the chemistry of ZIF-8, by investigating how the nature of ZIF-8 degradation differs in PBS and LB in terms of the rate and the final products and by understanding the underlying degradation mechanism of ZIF-8 and ZnO in PBS and LB. All the experiments in the media were carried out in the dark to avoid photodegradation and photoactive effects. The study demonstrated ZIF-8 as a superior candidate material for antimicrobial applications than ZnO. It was found that ZIF-8 works as a stronger antibacterial agent, even under dark conditions; it requires a lesser dosage and has a faster bactericidal rate. The superior antibacterial properties of ZIF-8 over ZnO were found to be directly associated with the differences in their stability in the respective culture media. Thus, this

study presents the first mechanistic investigation of the stability of ZIF-8 in cell-culture media. These observations and the combined analytical methods will provide guidelines to re-examine the stability of MOFs in biomedical and environmental applications. This study also provides valuable insights regarding the degradation of micro/nanoparticles in culture media and their subsequent impact on bacteria.

## 5.4 Experimental Procedures

### 5.4.1 Synthesis of ZIF-8 NPs

ZIF-8 powders were synthesised via a mechanochemical route as reported elsewhere [24]. The reagents, zinc acetate (Sigma-Aldrich) and 2-methylimidazole (HmIm, Sigma-Aldrich), with a metal-to-ligand ratio of 1:8 were placed in a stainless steel ball milling vial along with stainless steel balls of 8 mm in diameter. The ball to powder mass ratio was 10:1. Net molar amounts of HmIm and metal acetate were selected to be 16.64 mmol and 2.08 mmol, respectively. After 2 hours of milling in a Spex 8000 mixer/mill, 25 mL of DI water (18 mΩ) was added into the milling container and shaken for 15 minutes. The resulting powders were vacuum-filtered using a filter paper with an average pore size of 200 nm. Residual reactants were removed by washing the powder with DI water and then with ethanol. Subsequently, the powders were dried at 50 °C overnight in air. The dried powders were subjected to heat treatment at 150 °C for 2 hours to remove the guest molecules trapped in the pores of the ZIF structure. Reagent grade ZnO powders with an average particle size in the range of 200-400 nm (Sigma Aldrich) were used as a benchmark nano-particulate antibacterial agent.

### 5.4.2 Materials Characterization and Degradation Study

Scanning electron microscopy (SEM, Zeiss Ultraplus FESEM, Germany) was utilised to image the morphology of the powders and bacteria exposed to powders, at an accelerating voltage of 2 kV. SEM analysis was preceded by a platinum coating of the samples to avoid

electrical charging. To prepare the SEM samples to study the interaction between the powders and the bacteria, the samples were fixed with 2.5% glutaraldehyde in a PBS solution for 2 hours. After placing them on poly-L-lysine-coated coverslips, the samples were washed step-wise with PBS, deionised water, different mixtures of deionised water and ethanol (10, 30, 50, 70, and 90 vol% of ethanol), and finally with pure ethanol. Then, the samples in pure ethanol were dried using a supercritical dryer at 40 °C under 90 bar (Balzers CPD 030).

Powder X-ray diffraction (XRD) analyses were performed using a D2 Phaser (Bruker) to study the crystallinity of the powders. Thermogravimetric analysis (TGA) was carried out using a Netzsch STA 449 F3, in air using an alumina crucible. UV-Vis absorption spectra in a wavelength range of 190-800 nm were acquired using a Cary 60 UV-Vis spectrophotometer (Agilent) to trace the release of Hmlm. Concentrations of released  $\text{Zn}^{2+}$  ions in different media were recorded using an inductively coupled plasma optical emission spectrometry (ICP-OES) instrument (5110, Agilent), and a multi-element standard external calibration curve was employed to calculate the concentrations of zinc cations. Fourier-transform infrared spectroscopy (FTIR) spectra from 4000 to 400  $\text{cm}^{-1}$  were obtained using a Bruker ALPHA II Spectrometer with the ATR module.

### 5.4.3 Antibacterial tests

LB media were prepared by dissolving 10 g of tryptone (Bacto laboratories), 10 g of NaCl (Analytical grade, Thermo Fisher Scientific), and 5 g of Yeast extract (Merck & Co.) in a total 1 L of DI water and autoclaved [68]. Sterile PBS (Sigma Aldrich) was used for the experiments.

Ampicillin-resistant Gram-negative *E. coli* cells were cultured on LB agar containing 100  $\mu\text{g mL}^{-1}$  of ampicillin. All the cultured cells were incubated and initially diluted to reach an optical density (OD) value between 0.4–0.6 (log phase) at 600 nm. To study the toxicity in the

media, the culture was further diluted 1000 times to  $\sim 10^5$  cells mL<sup>-1</sup> using the respective media. For instance, to study toxicity and degradation in LB media, the log phase culture was diluted successively in LB media.

Examination of the antibacterial properties was carried out applying three different methods. As a preliminary study, a modified Kirby-Bauer method was used to assess the toxicity of the particles in the dry state. For this, powders of ZIF-8 and ZnO were uniaxially pressed into discs. The discs were then placed firmly on the agar plates which were uniformly covered with *E. coli*. The agar plates were then incubated at 37 °C and the zone of inhibition was compared after 24 hours.

Minimum bactericidal concentration (MBC) was quantified by the broth dilution method as discussed elsewhere [69]. ZIF-8, ZnO, and HmIm powders were dispersed in PBS containing  $\sim 10^5$  cells mL<sup>-1</sup> of bacteria, at powder-concentrations ranging from 75 to 1200 mg L<sup>-1</sup> with 75 mg L<sup>-1</sup> as the interval, in separate falcon tubes (total 10 mL of solution in each 15-mL-falcon tube). After 24 hours of incubation, the solution in each tube was serially diluted. The minimum concentration that produced no colonies on the plates is noted.

Dose-dependent bactericidal effects of the powders were studied using the plate dilution method. For this, ZIF-8, ZnO, zinc acetate dihydrate, and HmIm powders were dispersed in an LB medium containing  $\sim 10^5$  cells mL<sup>-1</sup> of bacteria in falcon tubes and then incubated at 37 °C. After 24 hours of incubation, the samples in each tube were plate-diluted and the number of live bacteria was determined. The use of the optical density method [70] to characterise the effect of powder-concentrations was not possible due to the opacity stemming from dispersed particles.

All the experiments were performed in the dark to avoid the effects of photocatalytic free radical generation [71–74].

## 5.5 Results and Discussions

### 5.5.1 Powder characteristics

Figure 5-1a-b show SEM images of as-received ZnO powders and as-synthesised ZIF-8 powders, respectively. ZIF-8 had the characteristic rhombic dodecahedron structure with particle sizes in the range of 200-400 nm. The commercial ZnO powder also had similar particle sizes. In this chapter, a commercial ZnO powder with particle sizes similar to that of synthesised ZIF-8 powders were intentionally selected as a benchmark nanoparticulate antimicrobial material, so that the discussion about the effect of particle size difference can be excluded in comparing their antibacterial properties and degradation characteristics [42,75]. XRD patterns of the powders are shown in Figure S 5-1 confirming the sodalite (SOD) and wurtzite structure of ZIF-8 and ZnO powders, respectively. It is noteworthy to mention that, after ball milling of the zinc acetate and Hmlm (molar ratio of 1:8) without any solvent,  $\text{Zn}(\text{Hmlm})_2$  metal-organic compound was obtained in a paste form [24]. When water was added, the ZIF-8 crystals grew freely in the aqueous media. This resulted in particles with well-defined geometrical-shapes and particle sizes similar to ZIF-8 powders synthesised by mixing aqueous solutions (Figure S 5-2).

### 5.5.2 Antibacterial properties

Figure S 5-3 displays the zone of inhibition formed around the ZnO and ZIF-8 discs. ZIF-8 registers an inhibition-zone diameter of  $20.1 \pm 0.7$  mm, significantly larger ( $p < 0.01$  in an unpaired student t-test,  $n=3$ ) than that of ZnO with  $14.6 \pm 1.2$  mm. Figure 5-1c shows MBC of ZIF-8 and ZnO powders in PBS. The MBC of ZIF-8 was significantly smaller ( $225 \text{ mg L}^{-1}$ ) than that of ZnO ( $600 \text{ mg L}^{-1}$ ). Similar observations were made by the analysis in an LB medium at different concentrations for ZIF-8 and ZnO (Figure 5-1d); a higher bactericidal effect was observed for ZIF-8 than ZnO in LB. Bacterial cell reduction in  $\log_{10}$  in case of ZIF-8 was 4.07 at  $1000 \text{ mg L}^{-1}$ , which is larger than that of ZnO (i.e. 2.96) at the same

concentration. These results demonstrate a stronger antibacterial effect of ZIF-8 against *E. coli* as compared to ZnO, in both PBS and LB. Figure S 5-4 demonstrates the bactericidal efficacy of zinc acetate dihydrate as a source of zinc cations [76] in LB media. The results show a cell reduction of 4.79 in  $\log_{10}$  at  $1000 \text{ mg L}^{-1}$ , which is discussed further below along with the mechanistic study of ZIF-8 degradation in LB media (Figure 5-3)). The powder concentration required to kill the same percentage of bacteria was much higher in LB than that in PBS. This is most likely due to the presence of nutrition in LB for bacteria to multiply prolifically; in PBS, the lack of essential amino acids and sugars reduces the growth rate of the cells [68]. However, differences due to the degradation pathway of the antimicrobial agents and their degradation products can also not be ruled out [35], and will be elaborated upon below.

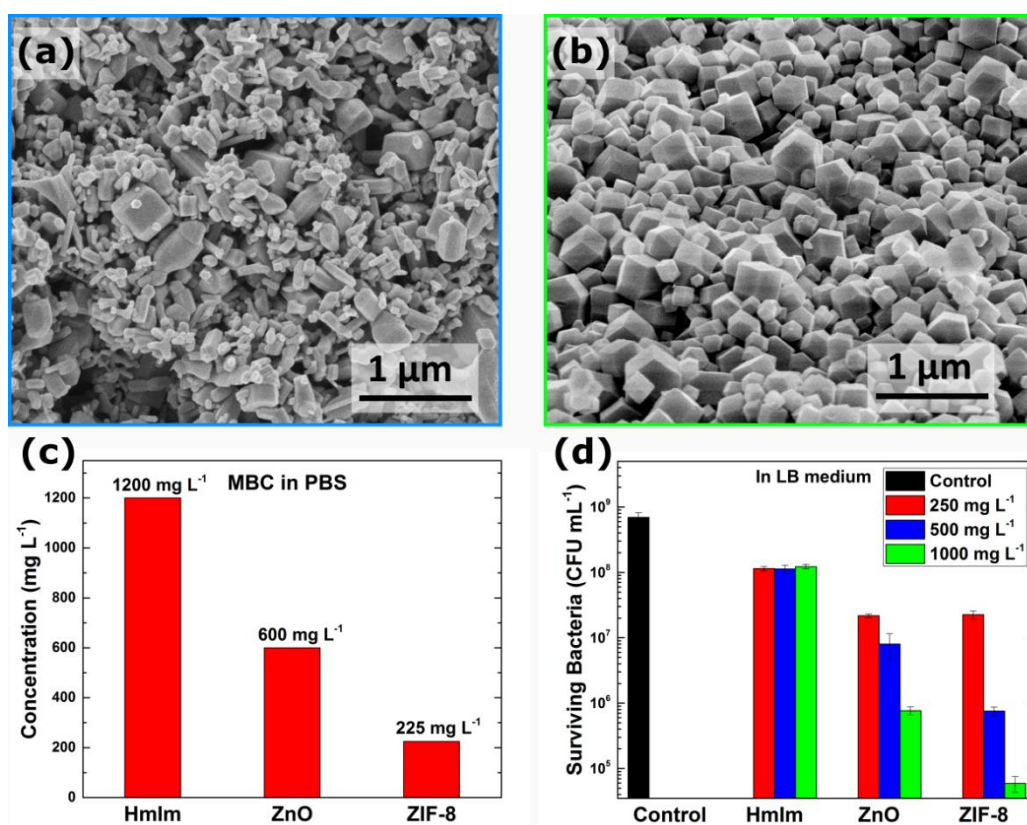


Figure 5-1 SEM images of (a) ZnO and (b) ZIF-8 nanopowders; (c) minimum bactericidal concentration ( $\text{mg L}^{-1}$ ) of Hmlm, ZnO, and ZIF-8 nanopowders in a PBS medium; (d) antibacterial efficacy of Hmlm, ZnO, and ZIF-8 nanopowders at 250, 500, and  $1000 \text{ mg L}^{-1}$  concentrations after 24 hours of incubation in an LB medium (\* represents  $p < 0.0001$  in an unpaired student t-test,  $n = 6$ )

### 5.5.3 Interaction between *E. coli* and the powders in different media

Figure 5-2 shows the microstructure of the bacteria before and after 24 hours of treatment with 1000 mg L<sup>-1</sup> of ZIF-8 and ZnO in LB and PBS. Untreated *E. coli* shows the characteristic rod-shaped structure (Figure 5-2a) [63]. Figure 5-2b-c shows typical *E. coli* cells treated with ZIF-8 and ZnO powders in LB, respectively. In both cases, some of the cells were slightly more flattened and decomposed/distorted, as shown with arrows in Figure 5-2b-c, indicative of the antimicrobial effects of ZIF-8 and ZnO powders. A similar observation can be made on the cells treated with ZIF-8 and ZnO in PBS (Figure 5-2d-e). It was also found that there was no evidence of ZIF-8 particles along with *E. coli* in the images; however, ZnO particles were present around the bacteria cells implying the faster degradation of ZIF-8 compared to ZnO.



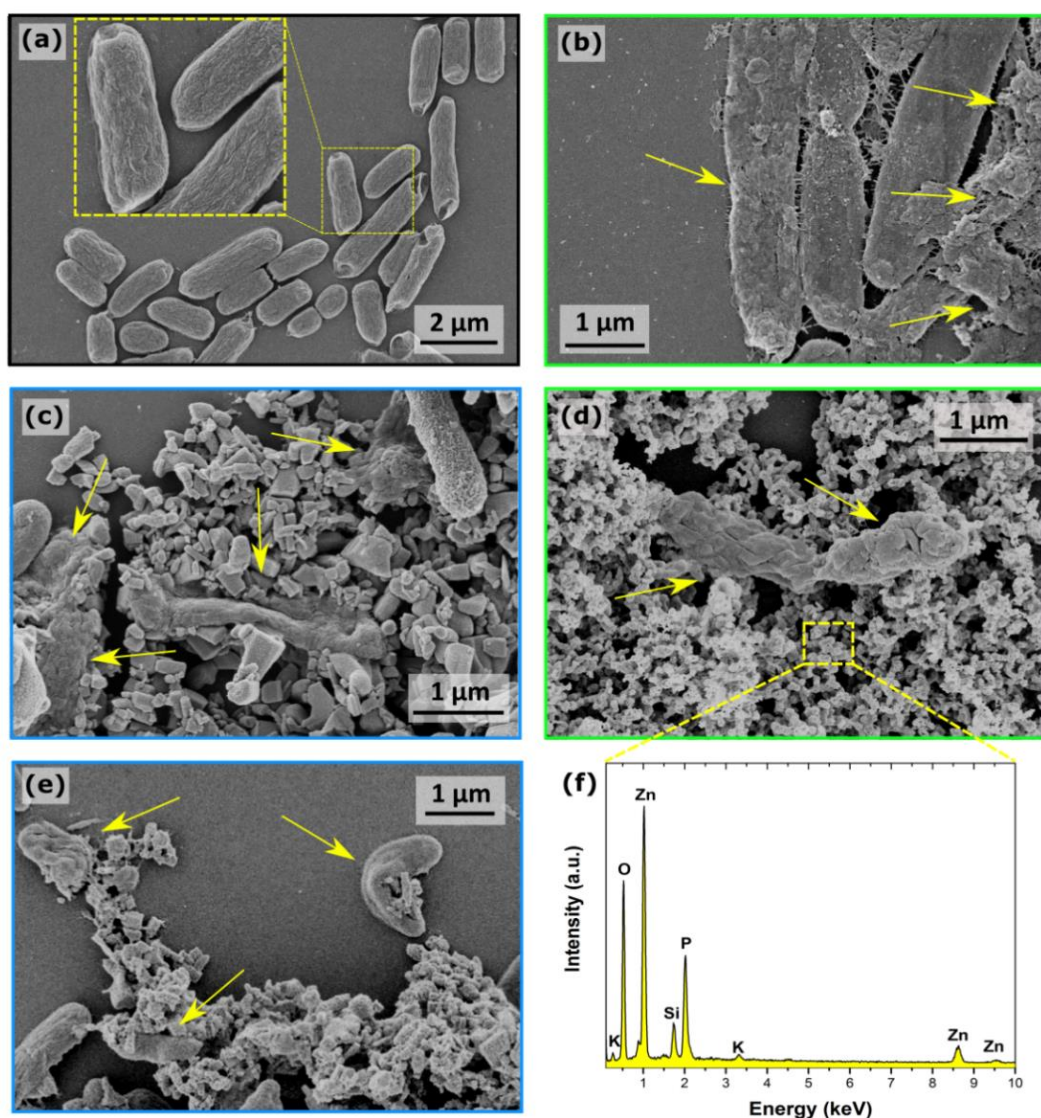


Figure 5-2 SEM images of (a) control *E. coli*; incubated *E. coli* in an LB medium in presence of (b) ZIF-8 and (c) ZnO nanopowders; incubated *E. coli* in a PBS medium in presence of (d) ZIF-8 and (e) ZnO nanopowders; (f) SEM-EDS analysis of the particles indicated in (d); Flattened and decomposed/distorted *E. coli* cells are indicated with arrows

#### 5.5.4 Powder degradation in bacterial culture media

Upon degradation, ZIF-8 releases both zinc ions and HmIm. Many studies showed that the release of zinc ions from zinc-based particles is responsible for their toxicity to bacteria [35,77–79]. The presence of Zn ions results in stress that deforms the cytoplasmic membrane of the bacteria. As a result, the shape of the cells changes [35]. The infiltration of Zn ions into the cell wall would cause cytoplasm leakage [35,77]. These factors lead to the

eventual death of the cell. However, the toxicity of Hmlm to bacteria is not well known. In the past, some imidazole-derivatives and their complexes were studied for antimicrobial applications but most of the studies did not include Hmlm [17,40,80–82]. In addition, few studies exploring the antibacterial effects of MOFs made with Hmlm, determined the effect of Hmlm alone [83]. In this chapter, MBC and the effects of dosage were studied not only with the synthesised ZIF-8 and commercial ZnO but also with Hmlm powders. As shown in Figure 5-1c and Figure 5-1d), Hmlm registered the lowest bactericidal effect among all three types of powders. In addition, Hmlm did not show a dose-dependent bactericidal effect, indicating that the lower count of surviving bacteria (Figure 5-1d) compare to the control (pH 7) was due to the increased pH (8-9) associated with the dissolution of Hmlm (Figure S 5-5) [84]. The results confirm a much weaker bactericidal effect of Hmlm than ZIF-8 and ZnO, indicating that the antibacterial effect of ZIF-8 is due to the released zinc ions, instead of the released and associated pH drop of Hmlm. To elaborate more on the antibacterial effect of zinc cations, the bactericidal efficacy of zinc acetate dihydrate as a source of zinc cations [76] was carried out (Figure S 5-4) in LB and is discussed further below. Differences in the antibacterial effects between ZIF-8 and ZnO were also attributable to the difference in stability between ZIF-8 and ZnO.

Next, the first mechanistic investigation of the stability of ZIF-8 in cell-culture media is presented. SEM images of bacteria samples treated with  $1000 \text{ mg L}^{-1}$  of ZIF-8 in LB, showed no evidence of ZIF-8 particles (Figure 5-2b). However, in the image of *E. coli* treated with ZnO powders (Figure 5-2c), an extensive presence of ZnO particles was observed. This implies faster degradation of ZIF-8 than ZnO in LB. The bacteria were then treated with ZIF-8 in PBS, discovering near-spherical nanoparticles (smaller than 100 nm, Figure 5-2d) with morphologies different from original ZIF-8 rhombic dodecahedron morphology with particle sizes in the range of 200-400 nm. The EDS analysis of the particles in the marked area of Figure 5-2d is shown in Figure 5-2f. The prominent peaks of Zn and phosphorus (P) suggest

that  $\text{Zn}^{2+}$  from the ZIF-8 structure reacts with the phosphate ions in PBS to form zinc phosphate [35,42].

To better understand the effect of different bacterial media on the toxicity of ZIF-8 to ampicillin-resistant *E. coli*, a quantitative study of the stability of ZIF-8 powders in comparison to ZnO powders was carried out. This was done first in the LB medium. The amount of degraded ZIF-8 and ZnO powders ( $\text{mg L}^{-1}$ ) are calculated based on the amount of  $\text{Zn}^{2+}$  ions in the filtrate detected by ICP-OES and the weight percent of  $\text{Zn}^{2+}$  ions in each powder (80.34 % in ZnO and 28.73% in ZIF-8) [24]. According to previous reports [35,85], it is assumed that the zinc cations are complexed with organic species in the LB medium to remain soluble and are not precipitating out as an inorganic salt. Figure 5-3a shows the amount of degraded ZIF-8 and ZnO as a function of powder concentrations (from 225 to  $1500 \text{ mg L}^{-1}$ ) in the LB medium. The amount of degraded ZnO did not show a strong dependence on the initial powder concentrations,  $\sim 130 \text{ mg L}^{-1}$  at all concentrations. The result is in agreement with Li's report where the release of  $\text{Zn}^{2+}$  from ZnO in LB saturates when the initial concentration of ZnO powder is greater than  $100 \text{ mg L}^{-1}$  [35]. In contrast, the amount of  $\text{Zn}^{2+}$  ions released from ZIF-8 increased steadily by increasing the initial concentration of ZIF-8 up to  $1500 \text{ mg L}^{-1}$ . Figure 5-3a also shows the amount of degraded ZIF-8 in weight percent that were converted from the measured amount of degraded ZIF-8 in  $\text{mg L}^{-1}$ , by dividing the measured amount of degradation ( $\text{mg L}^{-1}$ ) by the original concentrations of ZIF-8 in LB medium ( $\text{mg L}^{-1}$ ). The amounts of release correspond to 70-80 wt% degradation of the initial ZIF-8 powders in the 24-hour-time frame. The result supports the SEM observation (Figure 5-2b-c).

Considering the amount of ZIF-8 degradation after 24 hours in LB (70-80 wt%) and comparing their bactericidal efficacy in the same time frame (4.07 and 4.79 in  $\log_{10}$  at  $1000 \text{ mg L}^{-1}$  for ZIF-8 and zinc acetate dihydrate), the dominant antibacterial mechanism of ZIF-8 under a dark condition can be attributed to the release of zinc cations from its structure. It

should be noted that the weight percent of the zinc cation in zinc acetate dihydrate is 29.8 wt% which is similar to the weight percent of the zinc cation in ZIF-8 (i.e. 28.7 wt%).

The stability of ZIF-8 powders in LB in comparison to ZnO powders was further studied, by analysing the filtered powders after immersion in LB and washing with DI water, at the initial powder concentration of  $1000 \text{ mg L}^{-1}$ . A comparison of the normalised XRD patterns of the powders before and after immersion in an LB medium (Figure 5-3b) showed that most of the ZIF-8 powders were degraded, whereas ZnO powders were not altered, further supporting the calculated amounts of degradation in Figure 5-3a. The broad hump in the XRD patterns of filtered powders around  $25^\circ$  is indicative of the presence of amorphous moieties. FTIR spectra of the powders (Figure 5-3c) confirm that characteristic peaks of organic ingredients in the LB medium (a mixture of tryptone and yeast extract) are present in the spectra of the filtered powders. In fact, SEM images of the filtered powders (Figure 5-3d-e) show that the powders are covered by amorphous-like materials, as indicated with arrows.

It was found that washing the powders after filtration with ethanol, instead of DI water, could remove these organic moieties, resulting in better imaging of the filtered powders (Figure 5-3g-h). This washing process does not affect ZIF-8 and ZnO powders as they are stable in ethanol [86]. In the FTIR spectra of the filtered powders after washing with ethanol (Figure 5-3f), the peaks associated with organic ingredients in the LB medium are absent. In addition, the XRD patterns of the ethanol-washed filtered powders (Figure 5-3i) do not show the hump around  $25^\circ$ . These results confirm the success in removing the mentioned moieties. Figure 5-3h shows that ZnO powders retained their original morphologies (Figure 5-1a), which is consistent with their small degradation (Figure 5-3a);  $\sim 13 \text{ wt\%}$  at  $1000 \text{ mg L}^{-1}$  concentration). The XRD pattern and FTIR spectra of the washed powders show that some ZIF-8 powders remained in the filtered powder and they were still crystalline, though the particle sizes were reduced, and their shapes became rounder (Figure 5-3g) than

the original rhombic dodecahedron (Figure 5-1a). This infers the gradual dissolution of ZIF-8 from its outer surface (surface erosion) instead of internal pore surfaces (bulk erosion).

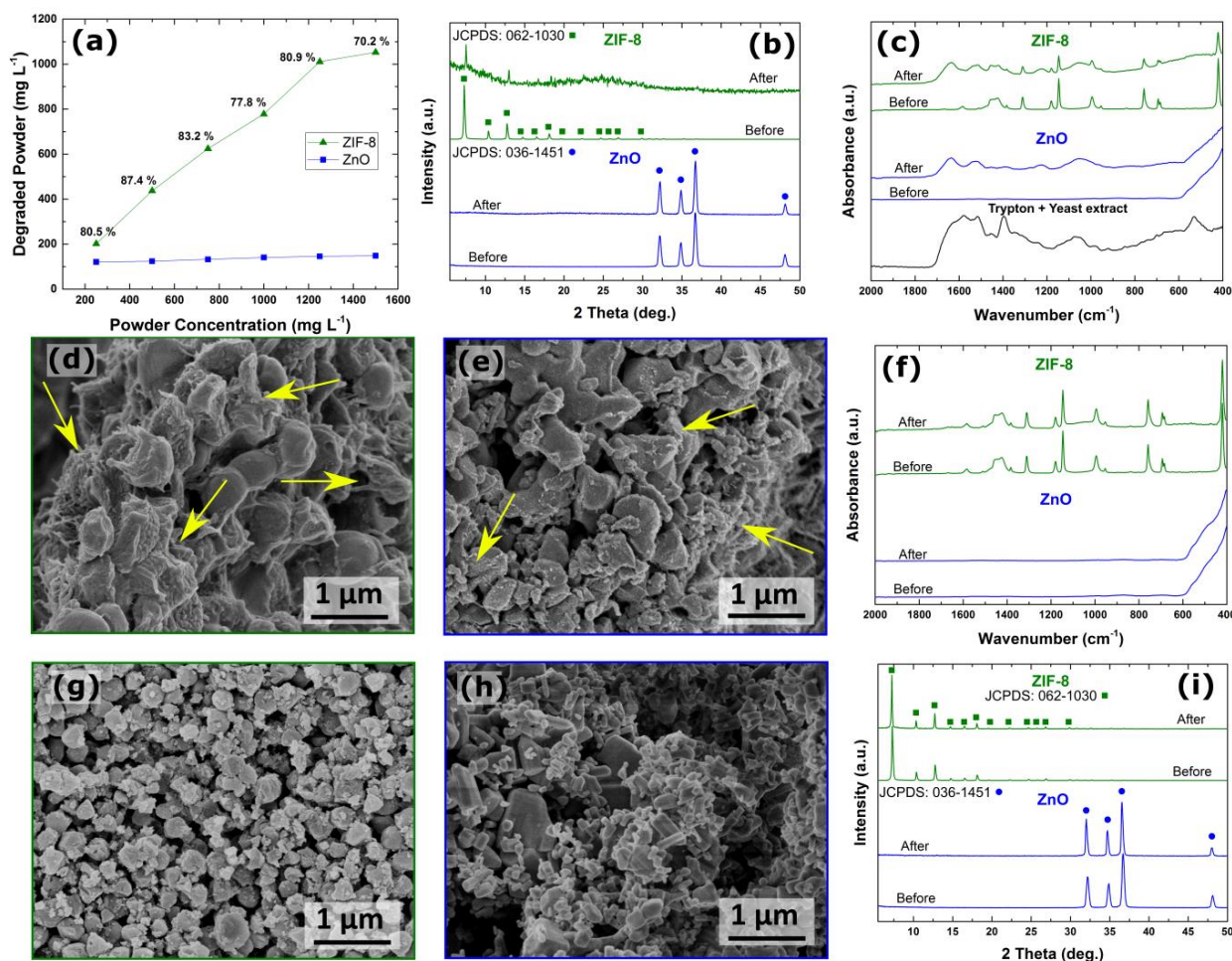


Figure 5-3 (a) Degradation quantity (mg L<sup>-1</sup>) of ZIF-8 and ZnO in an LB medium as a function of initial powder-concentration, calculated from the quantity of Zn<sup>2+</sup> in filtrate; (b) XRD patterns of filtered nanopowders washed with water; (c) FTIR spectra of the filtered ZIF-8 and ZnO nanopowders washed with water; SEM images of filtered (d) ZIF-8 and (e) ZnO nanopowders washed with water (the powders covered by amorphous-like materials are indicated with arrows); (f) FTIR spectra of the filtered ZIF-8 and ZnO nanopowders washed with ethanol; SEM images of filtered (g) ZIF-8 and (h) ZnO nanopowders washed with ethanol; (i) XRD patterns of filtered nanopowders washed with ethanol

Next, PBS, instead of LB, was used to conduct a quantitative study of the stability of ZIF-8 powders in comparison to ZnO powders. Figure 5-4a displays the calculated amount of degraded ZIF-8 and ZnO powders (mg L<sup>-1</sup>) in PBS, based on the released amount of Zn<sup>2+</sup> ions in the filtrate using ICP-OES. The results in Figure 5-4a suggest that the amounts of

degraded ZIF-8 and ZnO powders are negligible ( $1\text{--}2\text{ mg L}^{-1}$ , less than 0.7 wt% in the least concentrated samples i.e.  $225\text{ mg L}^{-1}$ ) and are independent of the initial powder concentrations. However, as discussed elsewhere [24,42], the amount of degraded ZIF-8 and ZnO powders cannot be accurately determined by measuring the amount of  $\text{Zn}^{2+}$  in the filtrates, if  $\text{Zn}^{2+}$  ions precipitate into solid powders as in the SEM image (Figure 5-2d) and are filtered out while collecting the filtrates. In such cases, the presence of Hmlm ligand in the filtrate of ZIF-8 can be used to measure the amount of the degraded ZIF-8, by UV-Vis absorption spectroscopy [24] (Figure S 5-6). As mentioned before, the synthesised ZIF-8 powders were subjected to heat treatment at  $150\text{ }^{\circ}\text{C}$  for 2 hours to remove the guest molecules trapped in the pores of the ZIF structure including the excess Hmlm. No weight loss was detected below  $300^{\circ}\text{C}$  in the TGA of the ZIF-8 powders (Figure S 5-7), confirming the absence of excess ligand in the structure. Thus, the presence of Hmlm in the filtrate can be attributed to the release of Hmlm from the ZIF-8 structure. By applying the Beer-Lambert law, the concentration of Hmlm in PBS can be determined from the optical absorbance at 206 nm, the peak position of a characteristic absorption peak of Hmlm [24]. The measured concentrations of Hmlm in  $\text{mg L}^{-1}$  are correlated to the amount of degraded ZIF-8 ( $\text{mg L}^{-1}$ ), knowing the weight percent of Hmlm in ZIF-8 (i.e. 71.27 wt%). The degradation in weight percent is calculated by dividing the amount of degraded ZIF-8 ( $\text{mg L}^{-1}$ ) by the initial concentration ( $\text{mg L}^{-1}$ ) of ZIF-8. It is to be noted that this method could not be used to study the degradation of ZIF-8 in LB because the optical absorption by LB (Figure S 5-8) masks the characteristic absorption peak of Hmlm at 206nm. The result in Figure 5-4b shows that 75-90 wt% of the ZIF-8 powder was degraded at all initial powder-concentration levels studied. In addition, the study of the degradation rate of ZIF-8 in PBS (Figure 5-4c) at the initial powder-concentration of  $1000\text{ mg L}^{-1}$  revealed that most of the degradation occurred in the first 4 hours, similar to the degradation of ZIF-8 in DI water [24]. It was also noted that the degradation rates of ZIF-8 powders synthesised using mechanochemical processing (MS) and solvent-based synthesis (SS) (Figure S 5-2) at the same initial powder-concentration are very similar in PBS. This confirms that the ZIF-8 powders used in this

study (synthesised via a mechanochemical method) have similar crystallinity compared to those prepared using the aqueous method.

The stability of ZIF-8 and ZnO powders in PBS was further studied, by analysing the filtered powders after immersion in LB and washing with DI water, at the initial powder concentration of  $1000 \text{ mg L}^{-1}$ . The SEM images of the filtered ZnO powders (Figure 5-4d) showed that ZnO retained its original morphology (Figure 5-1a), though particle surface was altered from a smooth surface into a rough surface. In contrast to ZnO, most of the ZIF-8 powders were converted into a powder with distinctively different morphologies from that of the original ZIF-8 particles. It can be attributed to a dramatic dissolution of ZIF-8 and precipitation of a new ligand-free structure. The formation of zinc-containing precipitates induced the low concentration of zinc ions (Figure 5-4a) and high concentration of Hmlm in the filtrate (Figure 5-4b).

As discussed earlier, SEM-EDS analysis of the precipitated particles after immersion of ZIF-8 in PBS showed that the precipitates contained zinc and phosphor (Figure 5-2f). The FTIR spectra of the filtered powders after immersion of ZIF-8 and ZnO (Figure 5-4g) showed broad bands at  $1200\text{--}900 \text{ cm}^{-1}$  and  $700\text{--}500 \text{ cm}^{-1}$  that can be ascribed to a  $\text{PO}_4^{3-}$  group [42]. These results suggest that the combination of zinc cations and phosphate anions precipitated as zinc phosphate compounds. However, the XRD patterns of the filtered ZnO and ZIF-8 powders (Figure 5-4f) do not show any extra peak, indicating that the precipitates may be amorphous, which impedes the identification of the precipitate by crystal-phase matching.

In order to identify the filtered powders, the powders were heat-treated and then examined by XRD. Figure 5-4h shows the TGA curves during the heat treatment in air. For both filtered powders, a small weight loss occurred up to  $350^\circ\text{C}$ , which is attributed to the elimination of water molecules from the hydrated zinc phosphate [87]. The filtered ZIF-8 sample showed a weight loss of 15.8 wt% between  $350$  to  $700^\circ\text{C}$ , due to the decomposition of the non-

degraded ZIF-8 into ZnO. The amount of weight loss was used to estimate the amount of the non-degraded ZIF-8 in the filtered powders [88], to be 24.6 wt%. This value is in good agreement with the amount estimated by the optical measurements of released Hmlm in Figure 5-4b (20.6 wt% at the concentration of  $1000 \text{ mg L}^{-1}$ ). XRD patterns of the samples after TGA measurements up to  $700^\circ\text{C}$  display the characteristic peaks of crystalline zinc phosphates in both samples, along with peaks associated with ZnO (Figure 5-4i). The results confirm that the amorphous nanoparticles precipitated in the ZIF-8 suspension in PBS are amorphous zinc phosphate hydrates which are also known antibacterial agents [89,90]. The intensities of the peaks associated with crystalline zinc phosphates are very weak in the ZnO sample, indicating negligible degradation of ZnO in PBS compared to that of ZIF-8. The SEM images in Figure 5-4d-e strongly support these results. The change of ZnO particles from smooth to rough surfaces (Figure 5-4d) may be attributed to the conversion of ZnO surface into nanostructured zinc phosphate.



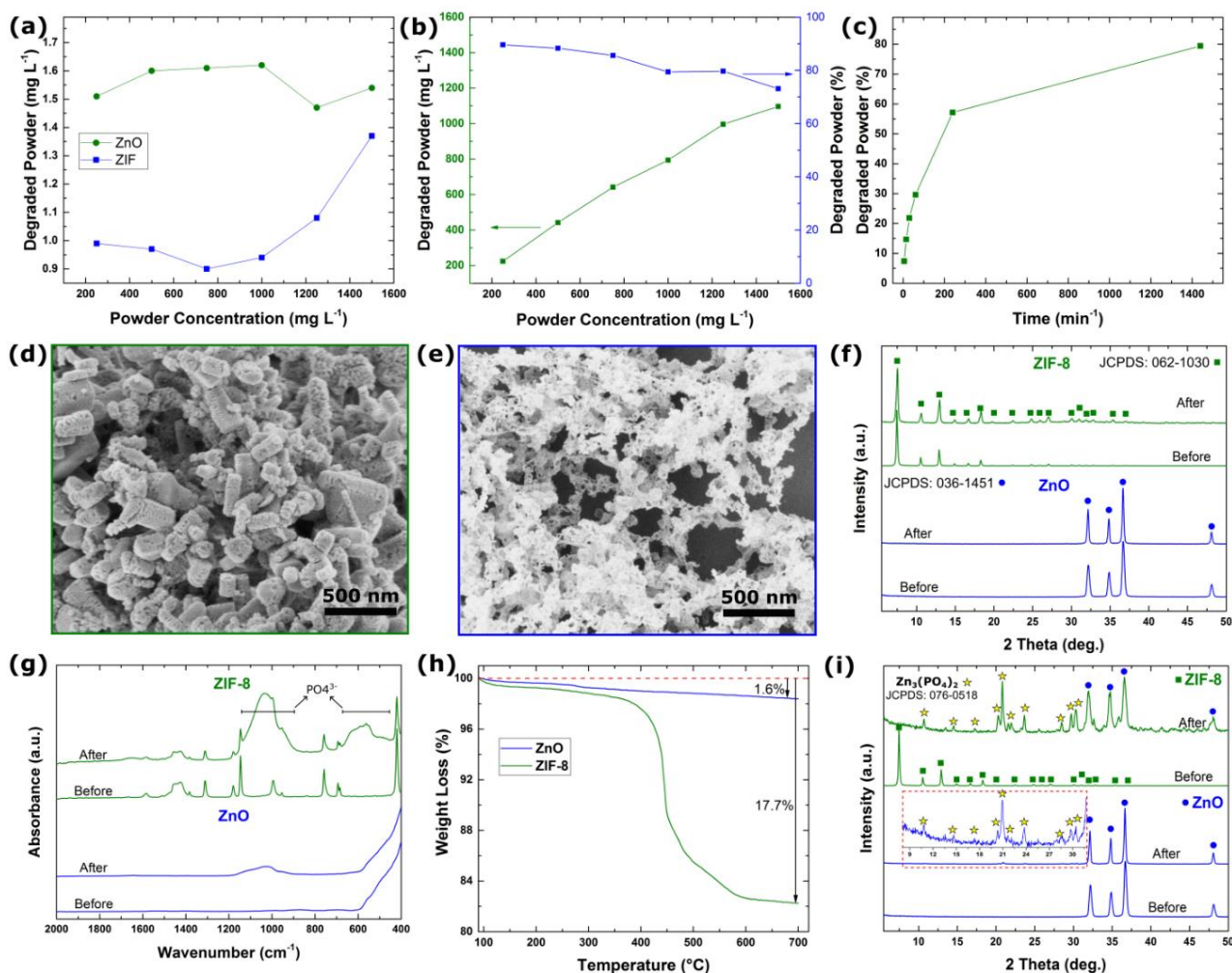


Figure 5-4 (a) Degradation quantity (mg L<sup>-1</sup>) of ZIF-8 and ZnO in PBS as a function of initial concentration, calculated from the quantity of Zn<sup>2+</sup> in the filtrate; (b) degradation quantity (mg L<sup>-1</sup> and %) of ZIF-8 in PBS as a function of initial concentration, calculated from the quantity of Hmlm in the filtrate; (c) degradation rate (%) of ZIF-8 in PBS as a function of immersion time; SEM images of the filtered (d) ZnO and (e) ZIF-8 nanopowders; (f) XRD patterns and (g) FTIR spectra of the filtered ZIF-8 and ZnO nanopowders; (h) TG curves of the filtered ZIF-8 and ZnO nanopowders up to 700°C, measured in air; (i) XRD patterns of the filtered ZIF-8 and ZnO nanopowders after TGA

### 5.5.5 Degradation equilibrium of ZIF-8

As reported in the previous chapter [24, Chapter 4], the degradation of ZIF-8 in water occurs in the first couple of hours and then slows down to reach an equilibrium. The amount of degradation depends on the initial powder-concentration in DI water [24]. A high initial powder-concentration results in only a small amount of degradation before reaching an

equilibrium, which could be a possible reason why many studies have not reported the aqueous instability of ZIF-8 [17,44,91–93].

At the initial powder-concentration of 1000 mg L<sup>-1</sup>, 22 wt% of the ZIF-8 nanopowders degraded in DI water after 24 hours of immersion (Figure S 5-9). At the same initial powder-concentration, the same ZIF-8 nanopowder in LB and PBS media underwent 70-80 wt% degradation in 24 hours. The higher amounts of degradation in LB and PBS than in DI water can be attributed to the presence of moieties in the bacterial media that has a high affinity to the released building block of ZIF-8 (i.e. Zn<sup>2+</sup> and mIm<sup>-1</sup>) such as phosphate ions in PBS and organic ingredient in LB.

In DI water, the hydration-deprotonation equilibrium can be expressed in the following equation:



where Zn(mIm)<sub>2</sub> is a unit building-block of ZIF-8. The affinity of the dissolved ions or molecules in the media towards the degradation product of ZIF-8, such as these:



can shift the degradation equilibrium (Equation 5-1) to the right side, by reducing the concentration of Zn<sup>2+</sup>. The reduced amount of free Zn<sup>2+</sup> and the toxicity of newly formed zinc compounds influence the overall toxicological effects of ZIF-8 in different media. This chapter revealed that ZIF-8 releases a higher amount of Zn<sup>2+</sup> than ZnO in these cell culture media, which resulted in a stronger antibacterial efficiency of ZIF-8 than ZnO.

The results of this chapter strongly advocate the importance of stability study on MOFs in developing their biomedical applications, in terms of their efficacy, bio-safety, and eco-

safety. It is also admonished that experimental results should be interpreted by considering the instability of MOFs in liquid media that leads to the release of MOF's building blocks and the subsequent formation of unwanted precipitation of the metal/ligand compounds. For example, the precipitation of released zinc cations as ZnO might be the reason why the bandgap of ZIF-8 in some studies [17,94] is reported to be  $\sim 3.3$  eV which is very close to that of ZnO, instead of values close to the theoretical bandgap of  $\sim 5.1$  eV [95,96]. The precipitation of ZnO would also inadvertently skew the antibacterial efficacy of ZIF-8 through its photocatalytic activities under UV light exposure [17]. This chapter also warns that, the stability of MOFs in liquid media cannot be determined by relying solely on the amount of free metal cations released from MOFs, if the dissolved metal cations form precipitates. For example, the additional antibacterial effect of the released ligand from dissolved MOFs, cannot be analysed correctly, if the amount of released ligand was indirectly estimated from the measured level of free metal cations in the media while ignoring the formation of precipitates from released metal cations [17].

## 5.6 Conclusions

This chapter demonstrates the antibacterial properties of ZIF-8, a zinc-based MOF, in comparison to ZnO, and establishes the former's superiority; a larger zone of inhibition ( $20.1 \pm 0.7$  mm for ZIF-8, against  $14.1 \pm 1.2$  mm for ZnO), a lower MBC value in PBS ( $250 \text{ mg L}^{-1}$  for ZIF-8, against  $600 \text{ mg L}^{-1}$  for ZnO), a higher bactericidal effect in LB (reductions of bacterial count in  $\log_{10}$  of 4.07 for ZIF-8, against 2.96 for ZnO, at a powder-concentration of  $1000 \text{ mg L}^{-1}$ ). ZIF-8, the most explored MOF in the ZIF family, possesses a number of other features beneficial to biomedical applications. Due to its framework structure, ZIF-8 can serve as vehicles to transport genes and drugs; ZIF-8 possesses high loading capacity, controlled release profiles, and biodegradability. The potential to exploit the multifunctional nature of ZIF-8 in biomedical applications makes it stand apart from other antibacterial agents based on metals and metal oxides.

The superior antibacterial properties of ZIF-8 in PBS and LB over ZnO were correlated with the stability of ZIF-8 and ZnO in these media. It was found that ZIF-8 degrades into different by-products when it is dispersed into different bacterial culture media. Importantly, the released zinc cations from both ZIF-8 and ZnO, the toxic agent against bacteria, precipitates out as amorphous zinc phosphates in PBS media, while it stays in LB media by complexing with the organic moieties. In addition, this work revealed that ZIF-8 degrades more and faster than ZnO in the cell culture media, which leads to superior antibacterial properties of ZIF-8 over ZnO against *E. coli*. Most of the ZIF-8 particles degrade in the first couple of hours after dispersion. A higher amount of ZIF-8 degrades in LB and PBS media (70-80 wt%) than in pure water (22 wt%). It can be attributed to the affinity of ions and organic constituents in the cell media towards the building block of ZIF-8, which influences the hydration-deprotonation equilibrium and enhances the degradation of ZIF-8.

These novel observations emphasise the importance of re-examining the stability of previously-considered-stable MOFs and their degradation behaviour in different media. For the successful use of MOFs in biomedical and environmental applications, there should be a clear understanding of how their chemistry varies according to the physicochemical properties of the environment. The choice of media significantly alters the experimental results which should be taken into consideration. The toxicity and stability of MOFs may vary in different media depending on the properties of the media. The re-examination of MOF's stability is also important from the viewpoint of bio-safety and eco-safety; as the number of industrial applications of MOFs increases, its discharge to the environment also increases. The findings and combined analytical methods in this work will provide valuable guidelines to the future quantitative investigation of the stability of MOFs in aqueous media and to study the effect of various ions and molecules in the media on their stability.

## 5.7 References

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## 5.8 Supporting Information

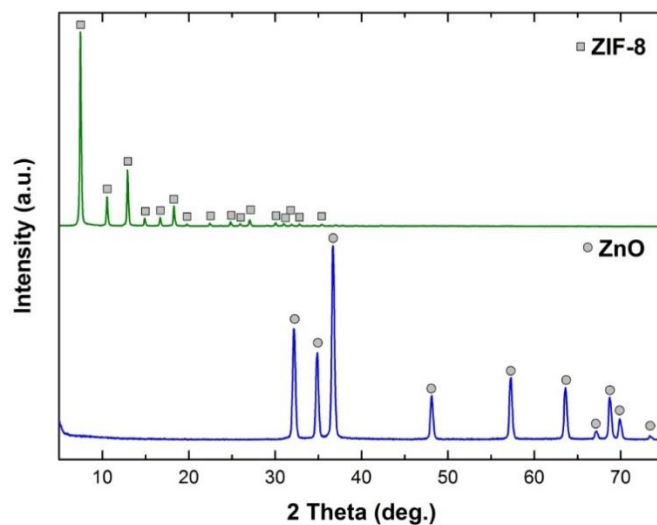


Figure S 5-1 XRD patterns of the commercial ZnO powders and as-synthesised ZIF-8 powders confirming the sodalite (SOD; JCPDS: 062-1030) and wurtzite structure (JCPDS: 036-1451) of ZIF-8 and ZnO powders, respectively

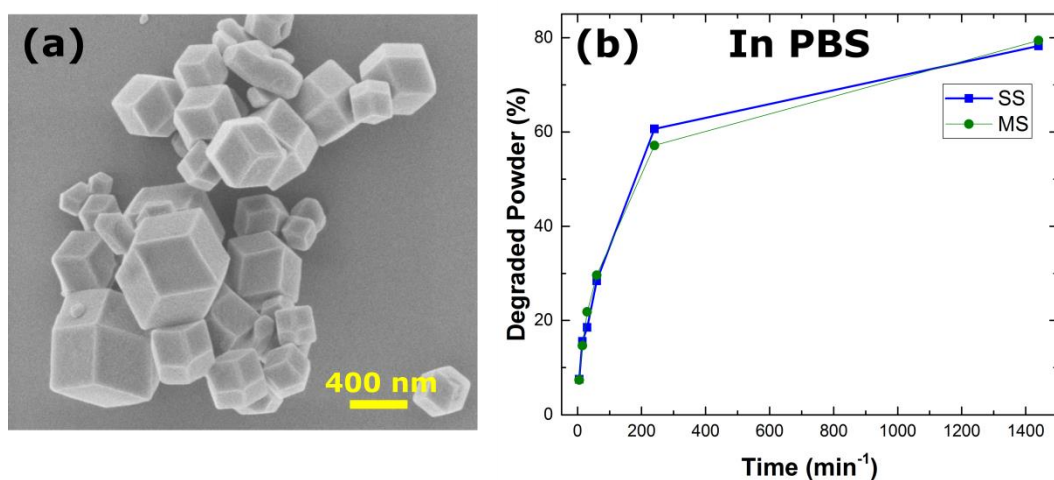


Figure S 5-2 (a) SEM image of ZIF-8 synthesised by mixing aqueous solutions of zinc acetate and 2-methylimidazole at a molar ratio of 1 to 8; (b) comparison of the degradation behaviour of ZIF-8 powders synthesised using mechanochemical processing (MS) and solvent-based synthesis (SS), in PBS at the initial powder-concentration of 1000 mg L<sup>-1</sup>.

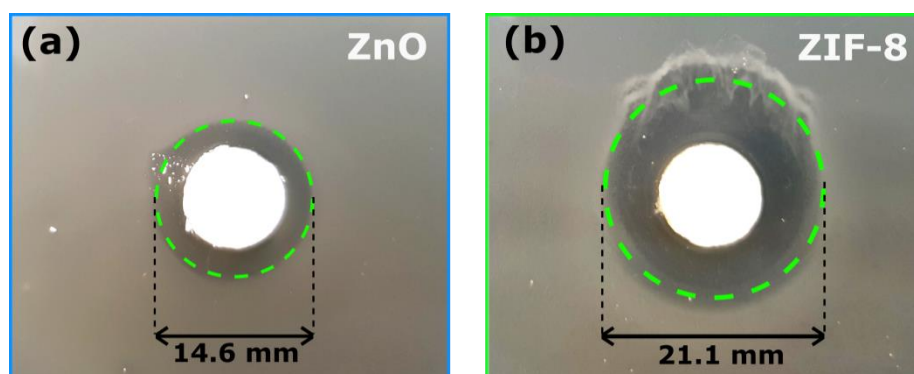


Figure S 5-3 Photographs showing zone of inhibition of (a) ZnO and (b) ZIF-8 nanopowders

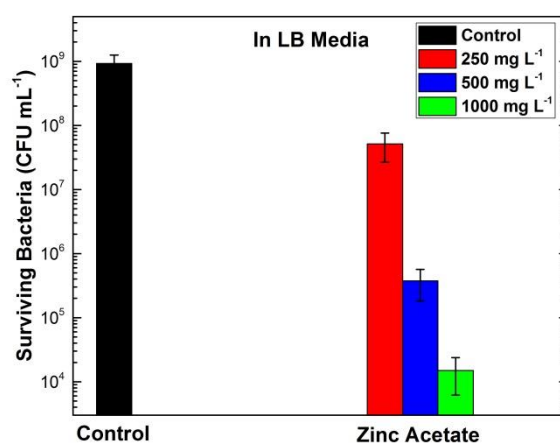


Figure S 5-4 Antibacterial efficacy of zinc acetate dihydrate at 250, 500, and 1000 mg L<sup>-1</sup> concentrations after 24 hours of incubation in an LB medium

**Note:** The weight percent of the zinc cation in zinc acetate dihydrate is 29.8 wt% which is similar to the weight percent of the zinc cation in ZIF-8 (i.e. 28.7 wt%).

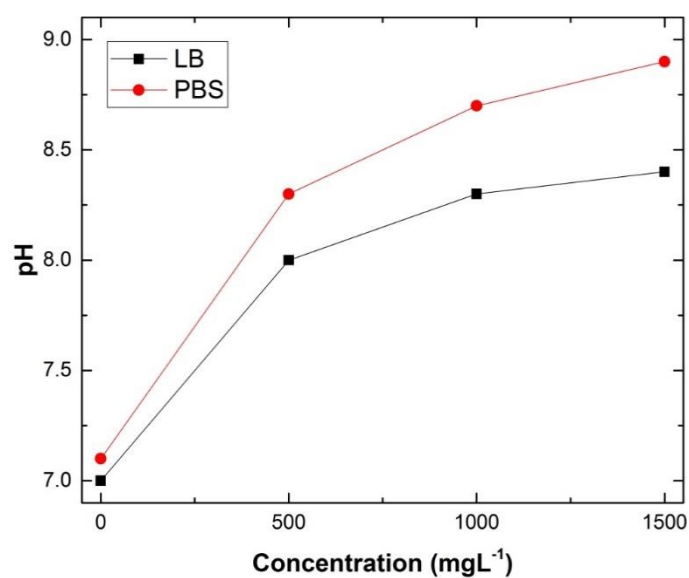


Figure S 5-5 pH of the LB and PBS media at different concentrations (mg L<sup>-1</sup>) of dissolved 2-methylimidazole

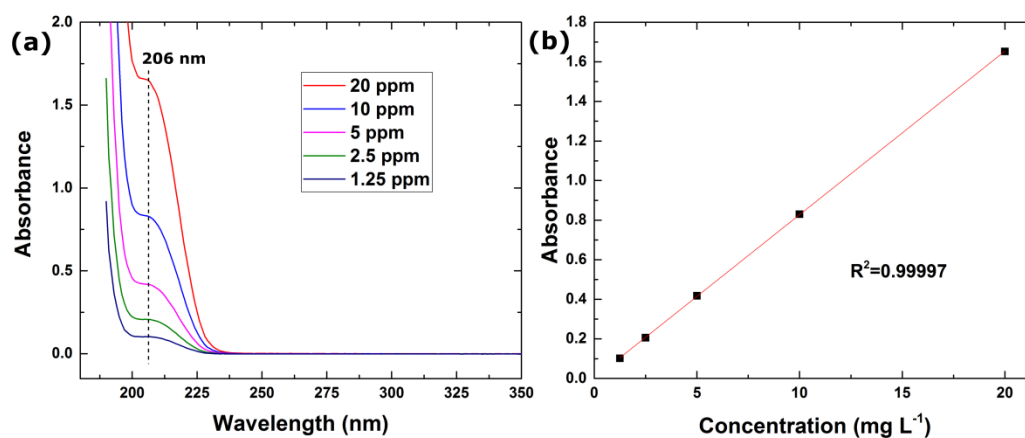


Figure S 5-6 (a) UV-Vis spectra of dissolved Hmlm in PBS at different known concentrations; (b) a calibration line for determining the unknown concentration of the Hmlm in PBS

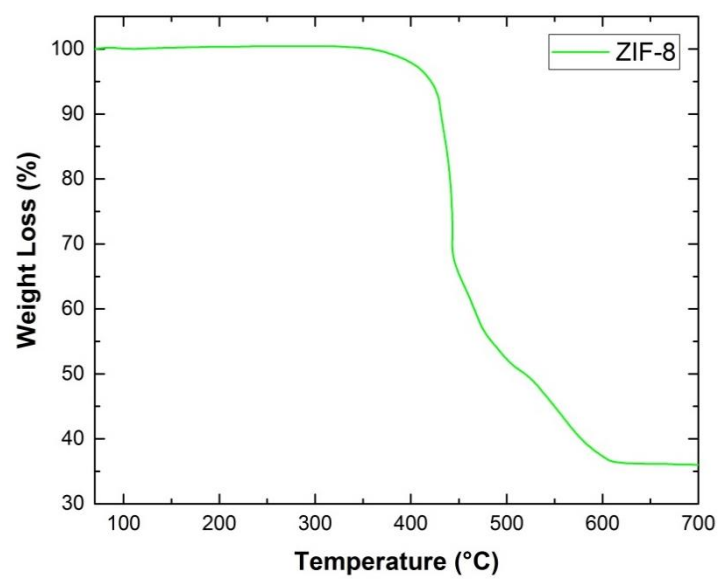


Figure S 5-7 Thermogravimetric analysis of the ZIF-8 powders

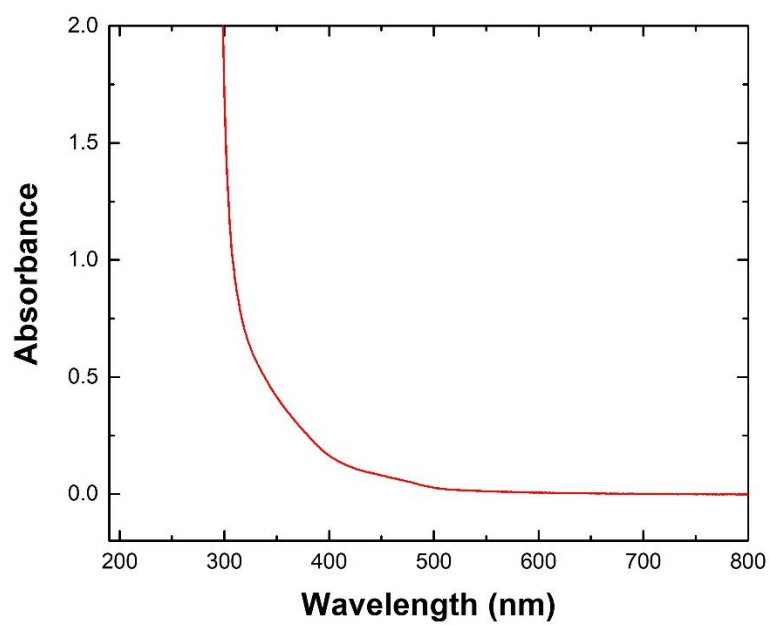


Figure S 5-8 UV-Vis spectrum of an LB media

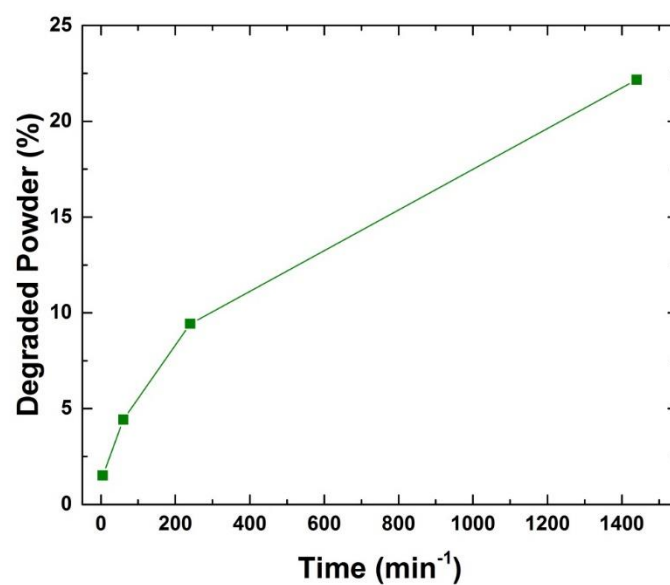


Figure S 5-9 Degradation rate (%) of ZIF-8 in DI water as a function of immersion time at the concentration of 1000 mg L<sup>-1</sup>



## **Chapter Five (Part II)**

### **ZIF-8 incorporation in Superhydrophobic Surfaces**

#### **5.9 Preamble**

This study is an extension to the investigation of the antibacterial properties of ZIF-8 powders. The study of ZIF-8 incorporation in superhydrophobic surfaces (SHSs) was carried out in collaboration with Mr. Deepu Ashok in Prof. David Nisbet's group at the Australian National University. The study about the preparation and antibacterial properties of SHSs without ZIF-8 incorporation was carried out by Mr. Ashok and details of the results can be found in Mr. Ashok's thesis [1]. The study about the preparation and antibacterial properties of SHSs with ZIF-8 incorporation was carried out by the candidate (Mahdiar Taheri) and Mr. Ashok who made equal contributions.

The mechanistic study on the durability of SHSs showed the limitations of SHSs in antibacterial applications: The loss of superhydrophobicity was observed after mechanical damages or long exposure to water, leading to the partial loss of antibacterial properties. This section of the thesis reports the incorporation of ZIF-8 into SHSs as a supplementary antibacterial agent, to overcome the limitations of SHSs in antibacterial durability. ZIF-8 was selected because of its good antibacterial properties as studied in the previous section of the thesis and also its intrinsic hydrophobicity with which the superhydrophobic nature of SHSs is not affected upon incorporation. In this study, sub-micron ZIF-8 powders were added to SHSs at the last stage of SHS preparation up to 20 wt% concentration, and their effects on the superhydrophobicity and antibacterial properties of the SHSs were investigated.

#### **5.10 Abstract**

Significant efforts are being directed at exploring novel methods to prevent bacterial adherence to surfaces. A durable superhydrophobic surface in the form of a coating has

been shown as a successful approach to impede biofilm formation on surfaces. Previously, the Australian National University developed a bioinspired hierarchical superhydrophobic surface (SHS). The SHS has a contact angle of  $157^\circ$  and a rolling angle of  $0^\circ$ . The SHS maintains superhydrophobic contact angles up to 100 cycles of rotary abrasion. The SHS reduced the adhesion of gram-negative *Escherichia coli* (*E. coli*) and gram-positive *Staphylococcus aureus* on its surface by 99.85 % and 99.94 %, respectively, in 10 minutes of submersion to aqueous bacterial suspensions. However, it was found that mechanical damages (i.e. scratches) and extended water-submersion result in the loss of superhydrophobicity, leading to bacteria adhesion and biofilm formation. To overcome the issue, this chapter investigated the inclusion of zeolitic imidazolate framework-8 (ZIF-8) particles in SHSs, whereby ZIF-8 imparts bactericidal properties post disruption of the superhydrophobicity of the coating. ZIF-8-incorporated SHSs retained their antimicrobial effect even after either significant coating damage or extended water-submersion for up to 9 days. The new type of coating may have a broad range of applications, including hospital infrastructure and food preparation facilities.

## 5.11 Introduction

Bacteria attach to surfaces and form immobilised multicellular communities called biofilms that inherently resist antibiotics and the immune system of hosts, causing persistent bacterial infections [2,3]. Gram-negative *Escherichia coli* (*E. coli*) and gram-positive *Staphylococcus aureus* are the most commonly found bacteria in biofilm infections [4]. The elimination of biofilms is generally difficult. Different strategies to combat biofilm infections include biocide-releasing, contact-killing, and bacteria-repelling surfaces [5]. Bacteria-repelling properties of surfaces can be attained by providing superhydrophobicity to the surfaces through the engineering of microstructures and surface chemistry [6].

On superhydrophobic surfaces (SHSs), water forms a droplet (with static water contact angles  $>150^\circ$ ) which rolls off easily (i.e. contact angle hysteresis  $<10^\circ$ ). The extreme water-repellent characteristic of an SHS is attributed to a combination of high roughness and non-wetting surface chemistry. The combination results in the formation of a Cassie-Baxter state where a thin air-film (called plastron) forms between the solid surface and liquid, preventing the liquid from wetting the solid [7,8]. A classic example of natural SHSs is lotus leaves [8]. Nature-inspired SHSs have attracted tremendous attention in the last decade due to their potential for a wide range of applications such as self-cleaning surfaces, blood repellent coatings, liquid and gas transports, and local drug delivery adjuvants [7,9–16].

Several investigations have been carried out on the bacterial colonisation onto SHSs [17]. The anti-biofouling properties of different SHSs and the decreased bacterial adhesion on SHSs are attributed to the high roughness of coatings and minimised contact area for bacteria [18–22]. Despite the advancement in fabrication techniques, the highly rough micro/nanoscale structures of SHSs suffer from inherent fragility towards abrasion, which limits their use in real-life applications [7,23].

Polymer materials such as polydimethylsiloxane and interpenetrating polymer networks (IPNs) can form excellent interfacial structures to hold nanostructures on surfaces, due to their excellent durability and strength [24,25]. At the Australian National University, an IPN of polyurethane (PU) and polymethyl methacrylate (PMMA) was synthesised and its excellent robustness and chemical resistance were demonstrated [1,26]. In the study, the IPN was sprayed on a surface to form a micro-rough-textured surface layer and subsequently, fluoro silica (FS), a known super hydrophobic compound, was sprayed on the IPN layer. This resulted in a hierarchical SHS which outperformed previous studies in terms of durability [9,15,26]. The mechanism of the bacterial repellency (the presence of plastron), the time dependence of the performance when exposed to a bacterial suspension, and the collapse mechanism of the antibacterial properties of the IPN-based SHSs were also investigated [1].

The study reported that immersion of SHSs in an aqueous medium for a certain time led to the occurrence of an air-film bursting phenomenon and an eventual increase in bacterial adhesion [1]. Although it is unlikely for the coatings to be immersed in water for a long period in many environments (e.g. hospitals), this structural instability limits the breadth of applications for SHSs. For example, in settings such as marine environments, liquid-membrane systems, or bathrooms, anti-biofouling surfaces that can tolerate prolonged submersion would be of extreme significance [27–29]. In addition, the antibacterial nature of SHSs was compromised under a mechanical breakdown of the superhydrophobic coating [1].

To address these issues in this chapter, zeolitic imidazolate framework-8 (ZIF-8) particles were incorporated into SHSs, to impart dual-functionality to the surfaces: It is expected that ZIF-8 adds a bactericidal function through the release of zinc ions, while maintaining the superhydrophobicity of the coatings (the bacterial-repelling function) in dry conditions. As discussed in Chapter 5 (Part I), ZIF-8 acts as a reservoir of  $\text{Zn}^{2+}$  ions to be antimicrobial [30,31]. The absence of hydrophilic functional groups in 2-methylimidazole (HmIm) ligand makes ZIF-8 hydrophobic [32] and thus the superhydrophobicity of the coatings is not affected upon ZIF-8 inclusion. The hypothesis here is that the release of  $\text{Zn}^{2+}$  ions, which kills fouling bacteria near the surface, is promoted by the hydrolysis-based degradation of ZIF-8 that occurs as a result of surface-wetting caused by mechanical damages or the air-bursting phenomenon that occurs during long water-immersion.

## 5.12 Experimental Procedure

A polymeric suspension of interpenetrating polymer networks (IPN of polyurethane–polymethyl methacrylate) and an acetone suspension of fluoro silica (FS) nanoparticles (particle sizes in the range of 7–9 nm and a powder concentration of  $20 \text{ mg mL}^{-1}$ ) were separately prepared [1,26]. To prepare the IPN suspension, 2.2 g of 1,1,1,-

Tris(hydroxymethyl)-propane was added to a mixture of acetone and xylene (100 mL of each) in a three-neck-flask while stirring. Then, 10 mL of polytetramethylene ether glycol and 3.57 mL of tolylene-2,4-diisocyanate were added to the mixture and was stirred for 30 minutes to start the polymerisation of polyurethane. After this, 10 mL of methyl methacrylate, 0.472 mL of trimethylopropane trimethacrylate, and 0.304 mL of 2,2'-azobis(2-methyl propionitrile) were added to the mixture. Next, 50  $\mu$ L of dibutyltin dilaurate was added as a catalyser. The flask was then sealed with rubber stoppers, attached to a condenser, and heated for 24 hours at 60 °C under a dark condition while stirring. The final IPN suspension had polyurethane : polymethyl methacrylate ratio of 64.75 : 35.25.

To prepare the FS suspension, 4 g of fumed silica powder was added to 160 mL of anhydrous chloroform. After adding 0.95 mL of Trichloro(1H,1H,2H,2H-perfluorooctyl)silane, the reaction container was sealed and stirred for 48 hours at room temperature.

It should be noted that the green synthesis of the SHSs was outside of the scope of this study.

Stainless steel 316L sheeting (2 x 2 cm<sup>2</sup>) were used as substrates and acrylic spray guns were used to spray the suspensions. On each side of the substrates, 5 mL of the IPN suspension was sprayed. After curing for 10 minutes, each side of the substrates was sprayed with 5 mL of the FS suspension to prepare the control SHS samples.

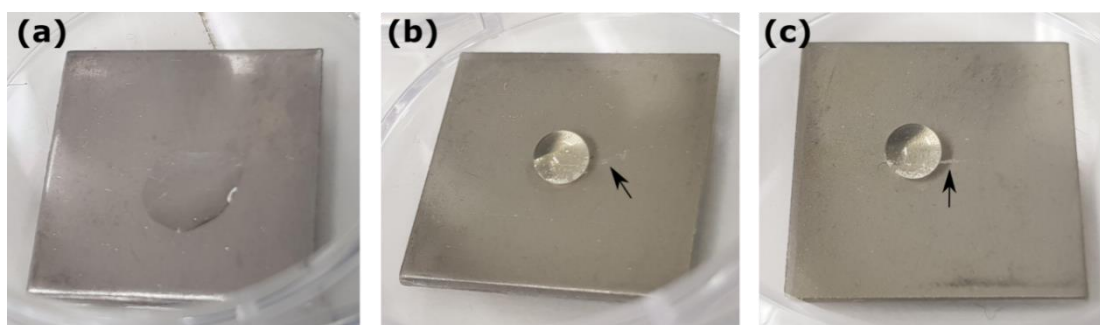
ZIF-8 powders were synthesised using the method in Chapter 4. For preparing the coatings containing ZIF-8 powders, ZIF-8 powders were added to the FS suspension at concentrations of 5 wt% (Z5), 10 wt% (Z10), 15 wt% (Z15), and 20 wt% (Z20) with respect to FS powders. The suspensions were ultrasonicated for 2 hours to finely disperse the particles. The coatings containing ZIF-8 powders were fabricated in the same way as the control SHS samples.

Field emission scanning electron microscopy (FE-SEM, Zeiss Ultraplus, Germany) was used to analyse the appearance of the coatings and morphology and distribution of the ZIF-8 particles within the coatings. Prior to SEM analysis, the samples were sputter-coated with platinum at 20 mA for 90 seconds. Static and rolling water contact angles were measured using a contact angle analyser (Surface Electro-Optics, Phoenix, Korea) by testing nine replicates in each test group. The coatings were characterised for the presence of ZIF-8 using an X-ray diffractometer (Bruker, D2 Phaser, USA) equipped with copper K $\alpha$  radiation with an average wavelength of 1.54059 Å. Fourier transform infrared–attenuated total reflectance (FTIR-ATR, Bruker-Alpha, USA) spectroscopy was used to record the absorbance spectra of the coatings.

The antibacterial properties of Z5, Z10, and Z15 coatings were studied, along with pristine SHSs and bare steel substrates as controls, under wet conditions: The samples were immersed under 5-cm-height of a cell culture medium containing  $10^3$ – $10^4$  cells mL<sup>-1</sup> of *E. coli*, and incubated at 37 °C for 1, 5 and 9 days. Then, 1 mL of the medium was taken out from above each sample, and the number of live bacteria in it was determined using the plate dilution method.

In order to investigate the antibacterial properties of the coatings under mechanical damages, a scratch was made in a fixed length on each SHS and Z15 coating towards the centre of the sample (indicated with arrows in Figure 5-5b-c) and a 20  $\mu$ L droplet of bacterial culture in log phase (with optical density value between 0.4 and 0.6 at 600 nm) was anchored at the centre. Pristine SHSs and bare steel substrates were used as reference samples. On the scratched coatings, the droplet remained anchored on the surface (Figure 5-5b-c). On pristine SHSs, the droplet immediately rolled away due to the small rolling angle. On bare steel substrates, the droplet spread on the surface due to the hydrophilic nature of the surface (Figure 5-5a). The droplets were left on the surfaces for 10 minutes, and then the surfaces were washed three times with PBS. Each cycle of washing

had 1 mL of PBS pipetted onto the surface. The samples were then transferred to 6-well-plates (one sample per plate). To provide moisture for the bacteria attached on the surfaces to survive, droplets of PBS were added around the samples in the wells. The wells adjacent to the samples were also filled with PBS. After 24 hours of incubation at 37 °C, the samples were stamped on agar plates. The agar plates were incubated overnight and then imaged using an Axio Observer microscope (ApoTome.2, Carl Zeiss, Germany).



**Figure 5-5** Photographic images of bacterial droplets on different samples; (a) bare stainless steel as a control, (b) scratched SHS coating, and (c) scratched SHS coating containing 15 wt% of ZIF-8. Black arrows indicate the scratches.

## 5.13 Results and Discussions

First, the physicochemical properties of the SHS coatings were studied. Figure 5-6a shows a typical SEM image of the ZIF-8 powder incorporated in the film (particle sizes in the range of 200–400 nm with rhombic dodecahedron morphology). Table 5-1 and Figure 5-6b show the contact- and rolling angle values of the coatings incorporated with different amounts of ZIF-8 powders. Sample Z5 registered the highest contact angle of 161°, higher than the control SHS sample (Z0). An increase in the amount of ZIF-8 resulted in a slight decrease in contact angle. The rolling angles of all samples were zero except for sample Z20. It is hypothesised that increasing the concentration of ZIF-8 in the coating, up to a certain limit, creates an additional degree of roughness which increases the contact angle [33]. Once the concentration exceeds the limit, hydrophobic ZIF-8 particles start being exposed on the superhydrophobic surface, leading to a decrease in contact angle and an increase in rolling

angle (pinning the droplet on the surface). Due to the lack of superhydrophobic properties of Z20, further studies were carried out without using Z20.

**Table 5-1 Contact- and rolling angle values of dual-functional coatings**

| Sample                    | Contact angle (degree) | Rolling angle (degree) |
|---------------------------|------------------------|------------------------|
| <b>Z0 (SHS)</b>           | $157 \pm 0.47^\circ$   | 0                      |
| <b>Z5 (5 wt% ZIF-8)</b>   | $161 \pm 4.67^\circ$   | 0                      |
| <b>Z10 (10 wt% ZIF-8)</b> | $158 \pm 1.41^\circ$   | 0                      |
| <b>Z15 (15 wt% ZIF-8)</b> | $155 \pm 0.66^\circ$   | 0                      |
| <b>Z20 (20 wt% ZIF-8)</b> | $149 \pm 1.63^\circ$   | $8 \pm 1.72^\circ$     |

Figure 5-6c shows the XRD patterns of the coatings and as-synthesised ZIF-8 powders. The characteristic peaks associated with ZIF-8 (at  $2\theta = 7.30, 10.35, 12.70, 14.80, 16.40$ , and  $18.00^\circ$ ) appeared in the XRD patterns of Z5, Z10, and Z15, confirming the presence of ZIF-8 in the coatings. The peak at  $421\text{ cm}^{-1}$  in the FTIR spectra (Figure 5-6c) is attributed to the stretching mode of Zn-N bonds between zinc ions and Hmlm in ZIF-8 [34] and is visible in the FTIR spectra of Z5, Z10, and Z15, further confirming the presence of ZIF-8 in the coatings.



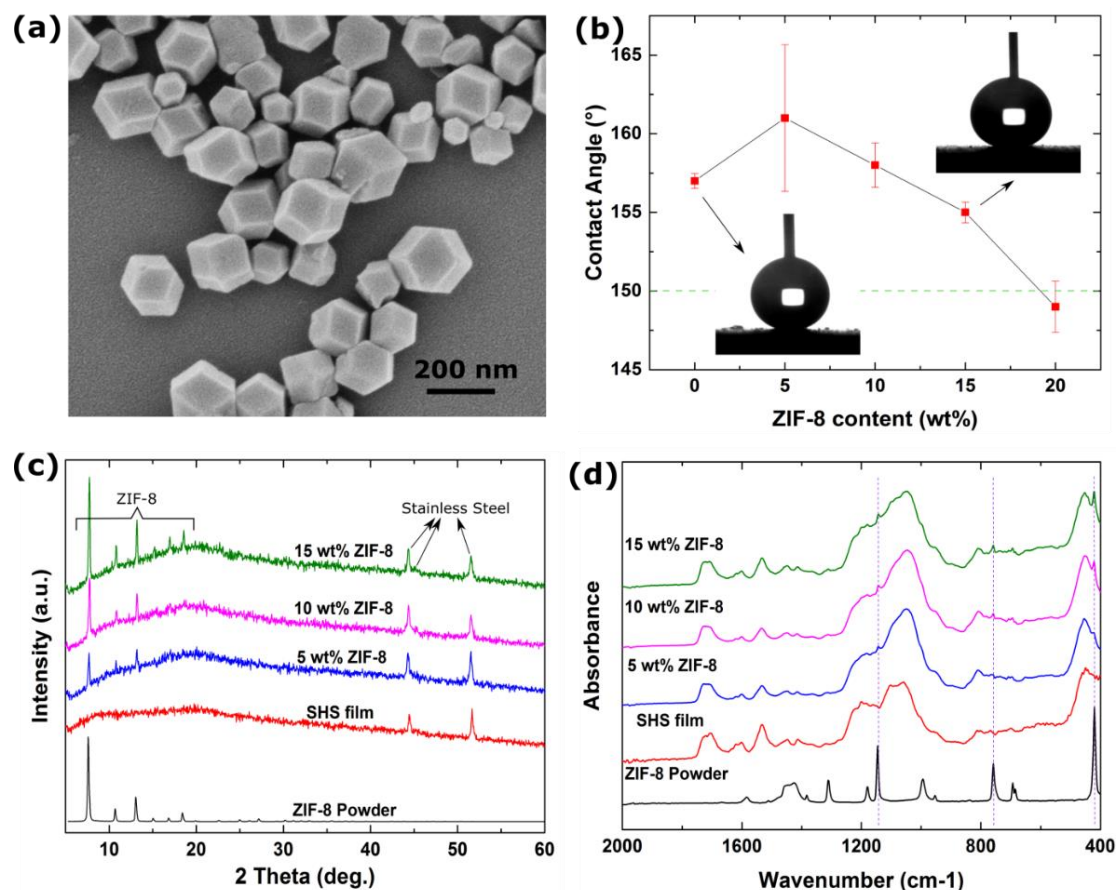
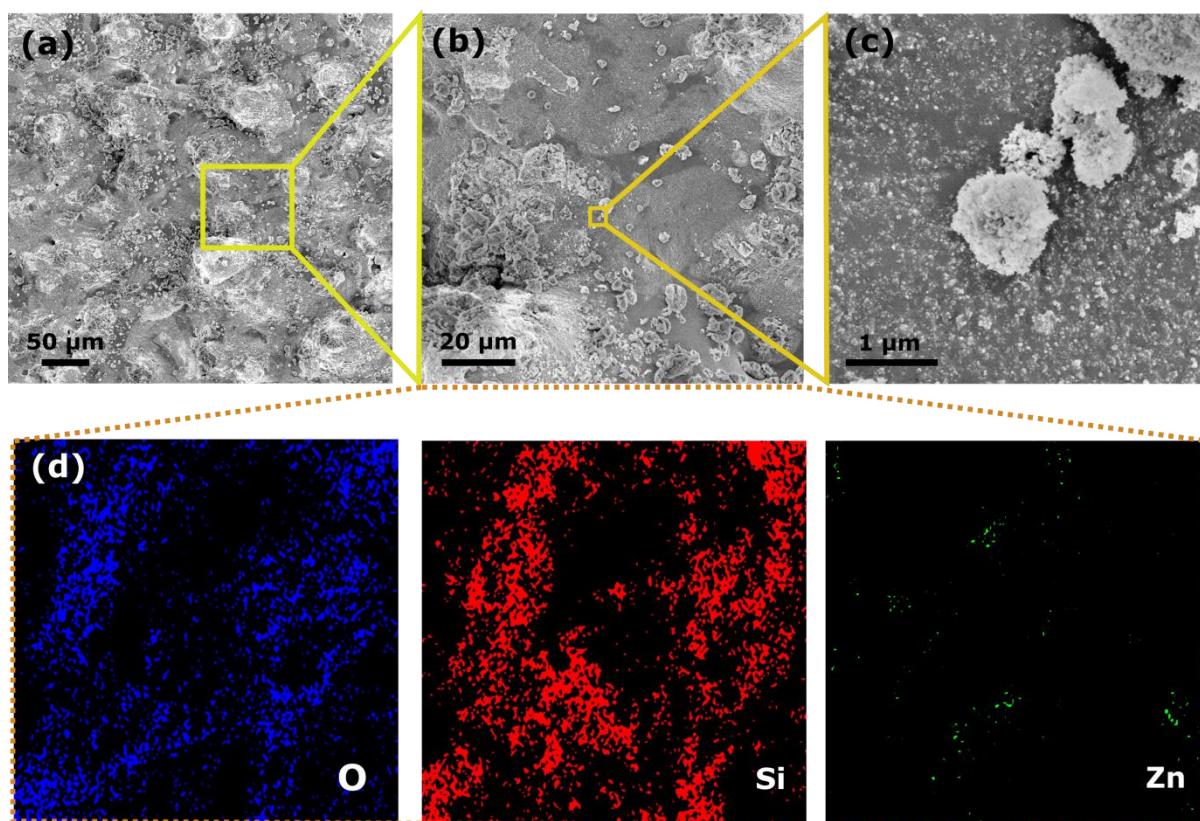


Figure 5-6 (a) SEM image of the ZIF-8 powders; (b) contact angles of SHS containing ZIF-8 powders (0-20 wt%); (c) XRD patterns, and (d) FTIR spectra of the coatings (SHS and the samples containing 5-15 wt% of ZIF-8 powders) on stainless steel in comparison with ZIF-8 powders.

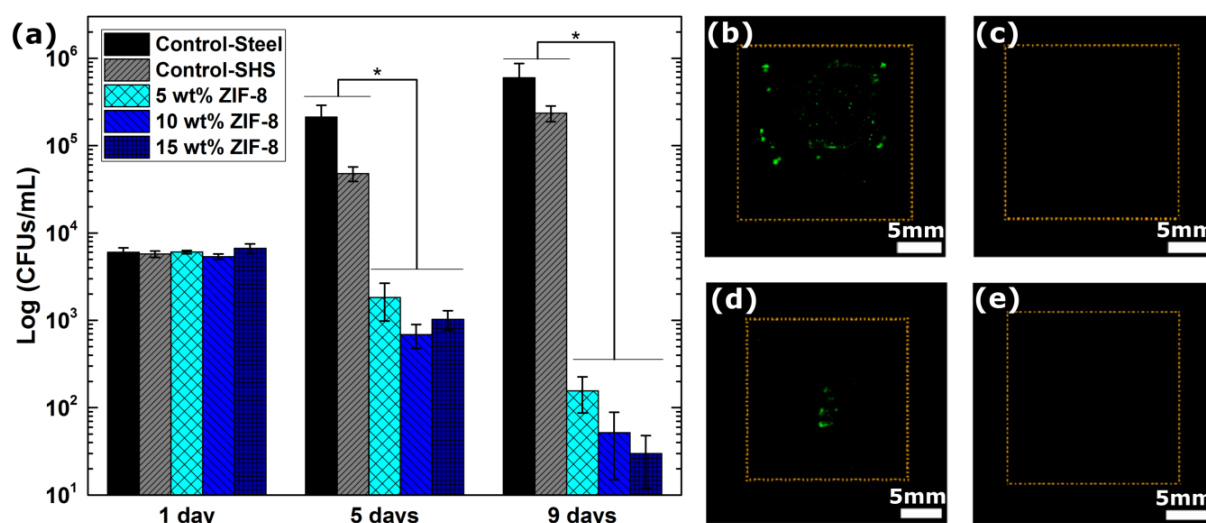
SEM images of the coating containing 15 wt% of ZIF-8 are shown in Figure 5-7a-c. Figure 5-7c depicts that ZIF-8 particles (200–400 nm) were covered by FS particles. EDX elemental mapping of the coating (Figure 5-7d) confirms the presence of zinc atoms that derives from ZIF-8 in the coating.



**Figure 5-7 (a-c) SEM images of the surface of a coating containing 15 wt% of ZIF-8 powders, at different magnifications, (d) EDX elemental mapping of the coating showing the distribution of oxygen, silicon, and zinc.**

To study the antibacterial properties of the coatings, un-scratched coatings were exposed to bacterial culture. The coatings were incubated under a 5-cm-column of bacterial culture containing  $10^3$ – $10^4$  cells  $\text{mL}^{-1}$  of *E. coli*. After 1, 5, and 9 days, live bacteria remaining in the suspension were quantified as shown in Figure 5-8a. Uncoated stainless steel and SHS (Z0) samples were taken as controls. After 1 day, there was no statistical difference between the controls and the test samples. After 5 days, the test samples with ZIF-8 (i.e. Z5, Z10, and Z15) showed a drastic reduction in cell counts. The control samples had an increase in cell counts due to the absence of biocides. After 9 days, the difference in cell counts between coatings with ZIF-8 and the controls, became more significant. Among the control samples, the SHSs displayed a slight reduction in the cell counts comparing to the uncoated stainless steel samples. This can be attributed to the release of FS nanoparticles into the suspension which kills bacteria by infiltrating the cells and consequential cytoplasm leakage [35,36].

Sample Z15 showed the highest reduction among the test samples due to the presence of more biocides (i.e. zinc ions) than the other samples [37]. The results indicate that the incorporation of ZIF-8 adds additional antibacterial functionality to the coatings. Once the plastron disappears, gradual wetting of the coating causes the ZIF-8 particles to decompose (Chapter 4 and 5 (part I)). This facilitates the release of bactericidal  $\text{Zn}^{2+}$  ions near the surface, thereby effectively prevent bacterial fouling in wet conditions.



**Figure 5-8 (a)** Antibacterial efficacy of the samples containing ZIF-8 powders after 1, 5, and 9 days using a plate dilution method (\* represents  $p < 0.001$  in an unpaired two-tailed student t-test,  $n=6$ ). Axio-observer images of the stamped agar; (b) control-steel, (c) pristine SHS, (d) scratched SHS, and (e) scratched SHS containing 15 wt% of ZIF-8

The dual-functionality of the coatings was further evaluated by mimicking possible mechanical damages to the superhydrophobic coating. In this experiment, the SHS and Z15 samples were deliberately scratched to introduce a defect in their superhydrophobic surface. The Axio-observer images of the stamped agar plates are shown in Figure 5-8b-e. The uncoated steel substrate showed a widespread adhesion of bacteria (Figure 5-8b). The pristine SHS sample, without any scratch, had no bacterial adhesion due to its superhydrophobic (bacterial-repelling) nature (Figure 5-8c). On the other hand, the scratched SHS sample with no ZIF-8 had bacteria attached on the defective region, as shown in Figure 5-8d. With the incorporation of ZIF-8 in the coating, no colony of the

bacteria was observed despite the scratch on the SHS (Figure 5-8e). When the plastron is eliminated by the mechanical damage, water makes contact with the surface of the coating. This prompts the hydrolysis of embedded ZIF-8 particles and the subsequent release of  $\text{Zn}^{2+}$  ions, which kills the adhering bacteria [3].

## 5.14 Conclusions

Recently, superhydrophobic surfaces (SHSs) have been investigated as an effective method to create antibacterial surfaces. However, their associated drawbacks, such as their metastabilities after long immersion under water or vulnerability to mechanical damages, have been limiting their applications. This chapter addressed these issues by incorporating ZIF-8 particles into SHS coatings while retaining the superhydrophobicity of SHS coatings. It was found that, by increasing the amount of ZIF-8 beyond 15 wt% (with respect to fluoro silica), the hydrophobic ZIF-8 particles start being exposed on the superhydrophobic surface, leading to a loss of superhydrophobic properties. SHSs containing up to 15 wt% of ZIF-8 were examined for antibacterial properties up to 9 days immersion under cell-culture media and in the event of a mechanical damage. After 9 days of immersion under culture media, the highest reduction in live bacteria counts (4.3 in  $\log_{10}$  with respect to a stainless steel control substrate) was recorded for the sample containing 15 wt% of ZIF-8, due to the presence of a high amount of biocides (i.e. zinc ions) in the film. Scratching the SHS sample with no ZIF-8 (as a possible mechanical damage) resulted in bacterial adhesion on the defective region. However, no bacteria colony was observed on the scratched sample containing 15 wt% of ZIF-8. The presence of ZIF-8 prevents bacterial growth by releasing  $\text{Zn}^{2+}$  ions (as biocides) at the locations where the superhydrophobicity broke down. The results of this study could assist future developments of antibacterial coatings to enhance health security.

## 5.15 References

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# Summary and Future Work

## 6.1 Summary

In this thesis, green and scalable synthesis approaches were explored for the potentially scalable production of zeolitic imidazole framework (ZIF) nanopowders and films. While minimising the environmental impacts of the ZIF's production, their microstructures were engineered to be used in sustainability-related applications, i.e. contaminant removal and energy storage. This thesis also provides a better understanding of the water stability of ZIF structures which is vital for their successful employment in water-based applications and enabled us to utilise ZIFs for other sustainable applications in the field of health security (as antibacterial powders and surfaces).

In the first study, ZIF-8 nanopowders were produced in a green and scalable way using a mechanochemical approach. The process parameters were studied to achieve a full conversion of ZnO raw material using a stoichiometric reaction, thus generating no wastage of raw materials. The advantage of using metal oxide starting materials in comparison with metal salts is that the by-product of the reaction is water, and there is no need to use organic solvents, additives, or extra ligand. In detail, liquid-assisted grinding for 8 hours and subsequent heat treatment at 180°C resulted in ZIF-8 nanoparticles of ca 80 nm in diameter with a low degree of agglomeration and a high surface area of 1885 m<sup>2</sup> g<sup>-1</sup>. Mechanochemically synthesised ZIF-8 nanoparticles had more adsorption sites for model organic pollutants than ZIF-8 made from a conventional methanol-based precipitation method. This was attributed to both the higher surface-to-volume ratio of nanoparticles and the higher number of surface-defect sites associated with their irregular shapes. This renders mechanochemically synthesised ZIF-8 an excellent material for the removal of both small (i.e. heavy metal ions) and large (i.e. organic molecules) contaminants at the same time.



In the second study, a flexible strategy to form tailored three-dimensional structures of ZIF films is presented. In this approach, highly porous films of ZnO nanoparticles were fully converted to uniform ZIF-8 films. The extrinsic porosities of the ZIF-8 films were tuneable, from a dense film to a hierarchically porous film. This was achieved by controlling the reaction temperature in the vapour-phase conversion of ZnO metal oxide precursor. Other unique advantages of this method include structural homogeneity, high scalability, and designable geometrical features. Using this method, dense films of ZIF-8 with intergrown grains were fabricated as robust self-standing monoliths without the need for binders. The ZIF-8 monoliths were tested as separators in lithium-sulfur batteries. Replacement of commercial polymeric separator with the ZIF-8 monolith resulted in enhanced long-term stability and performance of the battery system. The results showed that the crack-free ZIF-8 monolith is capable of blocking the migration and deposition of highly damaging polysulfide species (molecular sieving effect).

In the third study, a new understanding of the water stability of ZIF-8 and cobalt-doped ZIF-8 was obtained by using a new combination of several analytical techniques. The effects of ZIF concentration in water, cobalt doping level, and amount of extra ligands in water, on the water stability of ZIFs were investigated. This study showed that the analytical techniques previously used in the literature are not sufficiently sensitive to quantitatively detect the hydrolysis degradation of ZIF structures. It was demonstrated for the first time that UV-Vis spectroscopy can be used to quantitatively study the water stability of a wide range of MOF materials, as many common ligands in MOF structures can be detected in water by UV-Vis spectroscopy with high sensitivity. It was also shown for the first time that TGA analysis is capable of detecting the presence of metal-compound precipitates in the filtered ZIF powders as well as determining the minimum amount of additional ligands in water required to stabilise ZIF structures.

In addition, the study demonstrated a new mechanochemical ball milling method to synthesise highly crystalline cobalt-doped ZIF nanoparticles in the range of 200 – 400 nm. Unlike direct aqueous precipitation methods, this method allowed for the production of cobalt-doped ZIF-8 nanopowders with similar sizes irrespective of cobalt-doping levels. This enabled the study of the effect of cobalt-doping level on the water stability of ZIF-8, while eliminating the influence of particle size on water stability.

The fourth study demonstrates the antibacterial properties of ZIF-8, in comparison to ZnO, against *E. coli*. In this study, the instability of ZIF-8 in aqueous systems was exploited. The results showed the superiority of ZIF-8 over ZnO by recording a larger zone of inhibition, a lower MBC value in PBS, and a higher bactericidal effect in LB for ZIF-8. These features of ZIF-8 correlated with the instability of ZIF-8 in the bacterial culture media. ZIF-8 degrades more and faster than ZnO which leads to the release of more zinc cations, a well-known toxic agent against bacteria. It was also found that ZIF-8 degrades into different by-products when it is dispersed into different bacterial culture media. Importantly, the zinc cations released from both ZIF-8 and ZnO precipitate out as amorphous zinc phosphates in PBS media, while they stay in LB media in a soluble form by complexing with the organic moieties. Additionally, a higher amount of ZIF-8 degradation was observed in LB and PBS media (70 – 80 wt%) than in pure water (22 wt%). This can be ascribed to the affinity of ions and organic constituents in the cell media to the building block of ZIF-8 structure, which influences the hydration-deprotonation equilibrium and enhances the degradation of ZIF-8.

To explore the potential applications of ZIF-8 as an antibacterial agent, a study was carried out to incorporate ZIF-8 powders in a superhydrophobic surface (SHS) to supplement the antibacterial properties of the surface. SHSs were investigated as bacterial-repelling coatings to prevent bacteria adhesion and biofilm formation on surfaces. One of the drawbacks of the SHSs is its metastability after long immersion under water or in case of mechanical damages. The inclusion of ZIF-8 particles into the SHS introduced bactericidal

properties (biocide-releasing effect) while preserving the superhydrophobicity (bacterial-repelling effect). The coatings containing sub-micron-sized ZIF-8 particles were examined for antibacterial properties up to 9 days immersion under culture media and in the event of mechanical damage. The presence of ZIF-8 in the coatings prevent bacterial growth by releasing zinc ions (as biocides) when the superhydrophobicity breaks down, establishing dual-functional coatings.

This thesis has made multiple important contributions to the MOF research field. These include: (1) developing new green techniques to synthesise free-standing MOF nanoparticles and hierarchical MOF films, (2) obtaining a new understanding of the advantages and limitations in the green syntheses of ZIF-8 from ZnO, (3) demonstrating the ability to tune the physical properties of MOFs, including porosity, for a variety of sustainability-related applications, and (4) revealing the instability of ZIF-8 in different aqueous media and factors affecting the instability, using a new set of quantitative techniques. The scope of this work was limited to the ZIF family, primarily ZIF-8; however, the knowledge acquired in this thesis can be generalised into the synthesis, stability, and application of other members of MOF family.

## **6.2 Future Work**

Following the evaluation of the key findings, several avenues to further extend the present research are proposed below. These proposals target three aspects of MOF research: (1) green-synthesis of MOFs, (2) tuning and applying MOFs in other sustainability-related applications, and (3) water stability.

### **6.2.1 Mechanochemical synthesis of other MOF nanoparticles**

In the first study, ZIF-8 nanoparticles were synthesised from ZnO using a mechanochemical approach. This method can be extended to synthesising other types of MOF nanoparticles.

In the literature, MOFs have been produced from other insoluble metal oxides/hydroxides (e.g. MgO, Mg(OH)<sub>2</sub>, and Cu(OH)<sub>2</sub> [1,2]) using alternative synthesis methods. One main advantage of the mechanochemical approach is the ability to produce MOFs from simple and inexpensive metal precursors (i.e. insoluble oxides and hydroxides). This enables the green and scalable synthesis of MOF nanoparticles with unique surface chemistry. Future studies can include investigating the ability to produce MOFs, other than ZIF-8, from insoluble metal precursors using the mechanochemical synthesis method. This provides opportunities to further explore the advantages and limitations of this approach.

### **6.2.2 Dual adsorption of contaminants**

It was found in the first study that the ZIF-8 nanoparticles, synthesised via the mechanochemical method, have unique surface chemistry (surface defects associated with their irregular shapes) with a low degree of agglomeration. This provided more adsorption sites on their external surfaces for the removal of large contaminants (i.e. organic dyes). However, further studies on the adsorption of small contaminants such as heavy metals [3–6] (on the large internal surface) together with the large pollutants are required. This can highlight the dual-adsorption capability of mechanochemically synthesised ZIF-8 nanoparticles.

### **6.2.3 Gas adsorption and catalytic applications**

The findings in the second study can provide significant opportunities in gas adsorption and catalytic applications of ZIF films. It is shown that the extrinsic porosity of the ZIF films can be engineered by controlling the reaction temperature. However, the effect of this extrinsic porosity on the diffusion process of the gas molecules has not been investigated. The macro-porosity can improve mass transport and molecular accessibility, thus catalytic and adsorptive performances [7,8].

#### 6.2.4 Sensing application

Another advantage of the vapour-phase conversion of metal oxides to MOFs (second study) is the control over the final microstructure of the films. Flame spray pyrolysis can be designed to produce multilayers of metal oxide films such as ZnO/SiO<sub>2</sub>/TiO<sub>2</sub> [9]. The multilayers can be used as templates for selectively converting one of the metal oxide layers (e.g. ZnO) to the corresponding MOF layer (e.g. ZIF-8) by introducing the ligand vapour (e.g. 2-methylimidazole). The gas response of these heterostructures to volatile organic compounds (VOCs) can be of great importance in sensing applications [10,11].

#### 6.2.5 Using extra ligands to stabilise ZIF structures

ZIF-8 has been studied as a highly porous catalyst in water splitting and CO<sub>2</sub> reduction applications despite its instability in water [12,13]. It is shown in Chapter 4 that ZIF-8 can be stabilised in water by the addition of extra 2-methylimidazole and that the minimum amount of extra ligand required to stabilise ZIF-8 in water can be determined using thermogravimetric analysis (TGA). The applications of ZIF-8 in aqueous environments can be re-visited by the stabilisation of ZIF-8 with the addition of a necessary amount of 2-methylimidazole into electrolytes. The stability of ZIF catalysts should be analysed before and after the experiments using the new combination of analytical methods developed in Chapter 4. This will result in more accurate interpretations of ZIFs' catalytic performances in water splitting and CO<sub>2</sub> reduction applications.

#### 6.2.6 Effect of photolysis on ZIF stability

In the third and fourth reports, the water stability of ZIF-8 was investigated under dark conditions, eliminating any potential effects of light irradiation. In the literature, some studies were carried out in a closed environment without illumination [14,15], but many were under no controlled environment [16–21] presumably exposed to room light. As an extension to the third and fourth studies in the thesis, it was found that the irradiation of UVA, UVB, and near-

UV visible light accelerates the decomposition process of ZIF-8 in the presence of water [22]. However, the investigation into the mechanism of the light-accelerated decomposition has not been conducted. The study is of great importance because of the presence of light in most of the real-life applications of ZIF-8; ZIF-8 may be illuminated, either intentionally in photocatalytic applications or accidentally with sunlight or room light.

### 6.2.7 Re-examining the use of ZIFs as drug delivery vehicles

The last study showed the importance of re-examining the stability of previously-considered-stable MOFs and their degradation behaviours in different biological media. The successful use of a MOF in biomedical applications requires a clear understanding of how its chemistry varies according to the physicochemical properties of the environment. For example, ZIF-8 has been used as a pH-sensitive drug-delivery vehicle based on the assumption that it only degrades in acidic conditions [23,24]. However, the results presented in this thesis demonstrate that ZIF-8 degrades in neutral conditions (pH= ~7.4). This can cause “premature release” of loaded drugs, resulting in undesired toxicity instead of targeted release (acidic microenvironment). The findings in Chapter 5 can be used as guidelines to further investigate the stability of MOFs quantitatively in drug delivery applications.

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## Hierarchical Metal-Organic Framework Films with Controllable Meso/Macroporosity

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The structuring of the metal-organic framework material ZIF-8 as films and membranes through the vapor-phase conversion of ZnO fractal nanoparticle networks is reported. The extrinsic porosity of the resulting materials can be tuned from 4% to 66%, and the film thickness can be controlled from 80 nm to 0.23 mm, for areas >100 cm<sup>2</sup>. Freestanding and pure metal-organic frameworks (MOF) membranes prepared this way are showcased as separators that minimize capacity fading in model Li-S batteries.

### 1. Introduction

Metal-organic frameworks (MOFs) are extended materials consisting of inorganic nodes (metal clusters or ions) held together by multitopic organic linkers.<sup>[1,2]</sup> Their well-defined pore size,<sup>[2]</sup> tunable topology,<sup>[3]</sup> high accessible surface area, and chemical mutability,<sup>[4]</sup> make MOFs emerging materials for applications in gas storage,<sup>[5]</sup> separation,<sup>[6]</sup> catalysis,<sup>[7]</sup> biotechnology,<sup>[8]</sup> optics,<sup>[9]</sup> microelectronics,<sup>[10]</sup> and energy

production/storage.<sup>[11,12]</sup> However, for each application, MOFs need to be obtained in a suitable shape. For instance, while for gas storage applications synthesis and shaping of bulk powders is the most viable approach, other applications require the fabrication of MOFs as supported films or self-standing membranes. Moreover, while for the integration into microelectronics thin, smooth, and pinhole-free films are preferred, other applications benefit from coatings with a controllable interparticle porosity to ensure rapid mass transport (e.g., solid-phase microextraction<sup>[13]</sup> or chromatography).<sup>[14]</sup> Thus far, very few methods are available to deposit the latter type of mesoporous MOF films.<sup>[15]</sup>

Here, we report a protocol that uses oxide fractal nanoparticle networks (FNNs) as precursors for the binder-free shaping of MOF films. By tuning the oxide-to-MOF conversion, our approach enables to tailor the interparticle porosity. In general, the conversion of ceramic precursors to MOFs has shown to be an efficient route to fabricate films.<sup>[16,17,18]</sup> For instance, Ameloot and co-workers<sup>[17]</sup> demonstrated that ZnO films could be converted into ZIF-8 via exposure to a vapor of the 2-methylimidazole (2-MIM) linker. However, the conversion was limited to a depth of 15 nm from the top ZnO film surface. Instead of using dense oxide films, our approach leverages porous FNNs as 3D templates (Figure 1). Because of their high porosity, exposure of these FNNs to 2-MIM vapors results in their full conversion to MOF, while preserving the original fractal arrangement and advantages of solvent-free synthesis.

### 2. Hierarchical MOF Films

FNNs were prepared by the self-assembly of oxide precursor aerosols in the diffusion-limited cluster-cluster aggregation regime.<sup>[19]</sup> This approach is a scalable and reproducible route for the generation of materials with a fractal dimension ( $D_f$ ) of 1.7–1.8.<sup>[19]</sup> The thickness of the resulting film can be adjusted in the nano- to milli-meter range and depends linearly on the

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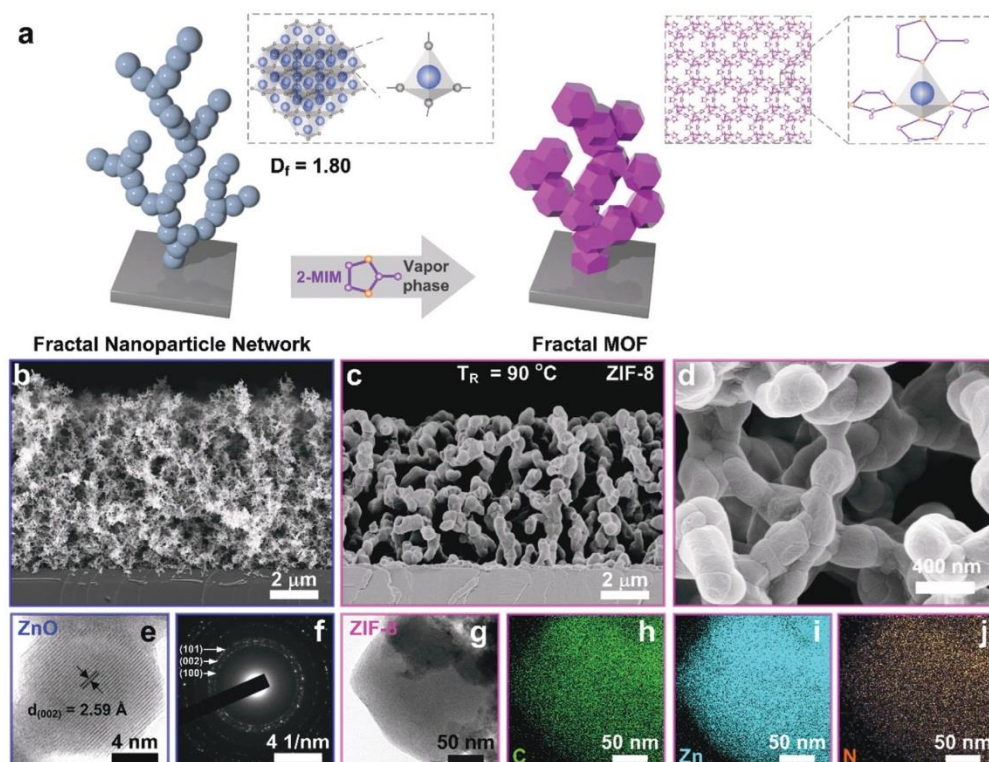
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**Figure 1.** Hierarchical MOF films through the conversion of fractal nanoparticle networks. a) Schematic representation of the conversion of a ZnO fractal nanoparticle network to ZIF-8, for a typical fractal dimension ( $D_f$ ) of the ZnO. b) SEM micrograph of a ZnO FNN and c, d) the resulting structured ZIF-8. e, f) HRTEM image and electron diffraction pattern of a ZnO nanoparticle detached from the network in b. g–j) HAADF-STEM image of a ZIF-8 particle detached from the network and elemental mapping. C, Zn, and N are represented in green, blue, and orange, respectively.

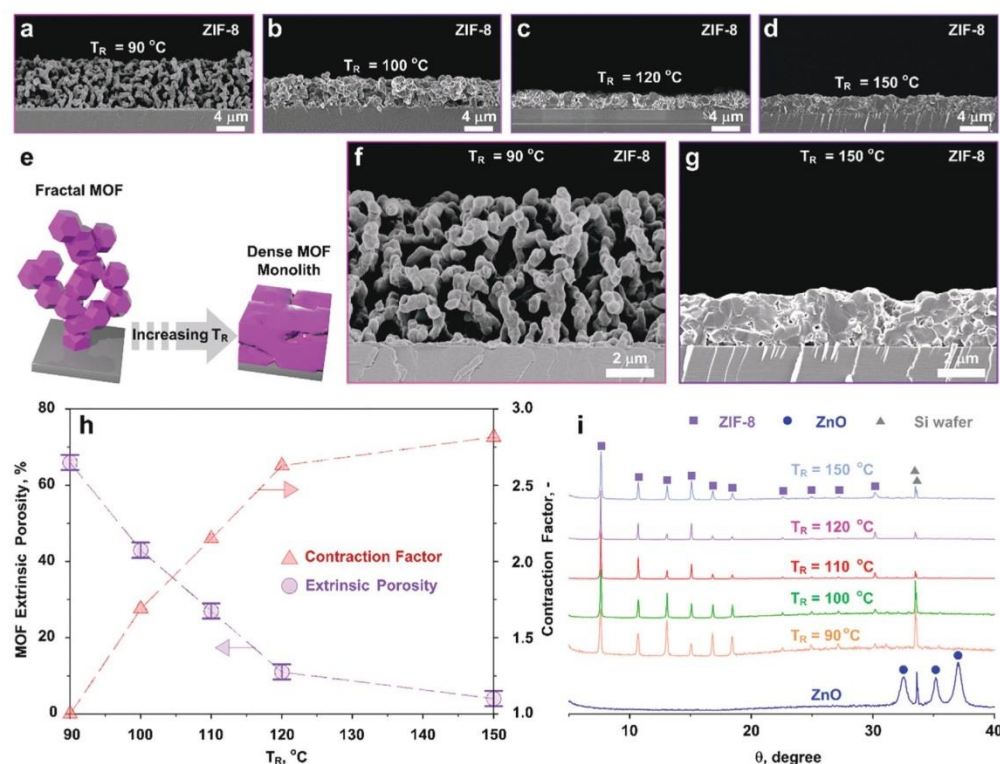
deposition time.<sup>[20]</sup> We used a liquid-fed flame synthesis reactor that permits the continuous synthesis of a broad range of metal oxide aerosols at a production rate up to  $1 \text{ kg h}^{-1}$ ,<sup>[21]</sup> and offers control over the nanoparticle size. Based on earlier reports,<sup>[17–18]</sup> we hypothesized that the particle size is a crucial parameter to achieve full ceramic-to-MOF conversion and optimized our method for the deposition of ZnO FNNs with primary particles smaller than 20 nm (Figure 1e, f, S1, Supporting Information).<sup>[22,23]</sup> Observations of the conversion of these ZnO FNNs by in situ synchrotron SAXS revealed a higher reactivity to 2-MIM compared to micrometer-sized ZnO powders (Figure S2, Supporting Information). In addition, the open fractal network was crucial for the full conversion into MOF (Figure S3–7, Supporting Information). Only for ZnO FNNs with an extrinsic porosity  $\geq 97\%$ , full conversion into crack-free ZIF-8 films was observed (Figures S5–9, Supporting Information). For lower porosity fractions, the volume expansion that occurs during the oxide-to-MOF conversion (10–17 times, depending on the ZnO crystallinity)<sup>[17,24]</sup> limits the diffusion of the ligand, resulting in

a partial conversion, residual stress, and cracks within the final MOF films (Figure S5, Equation 1, Supporting Information). The full conversion to ZIF-8 was confirmed by the absence of ZnO diffraction peaks (Figures S6, 7, 10a, Supporting Information) and FTIR spectroscopy (Figure S10b, Supporting Information). High-angle annular bright-field scanning transmission electron microscopy (HAADF-STEM) and elemental mapping confirmed the homogeneous distribution of carbon, zinc, and nitrogen in the ZIF-8 particles (Figure 1g–j). SEM analysis revealed that the texture of the resulting ZIF-8 films is dictated by the ZnO FNN precursor (Figures S11–13, Supporting Information) (Figure 1c, d). For instance, a ZnO FNN precursor with a fractal dimension ( $D_f$ ) of 1.8 and an accessible porosity of 98% yielded a ZIF-8 film with 66% of extrinsic porosity (Figure 1b–d).

### 3. Tuning the MOF Film Structure and Thickness

Our fractal-to-MOF conversion protocol allows to control the extrinsic porosity in the 4–66% range by controlling the reaction

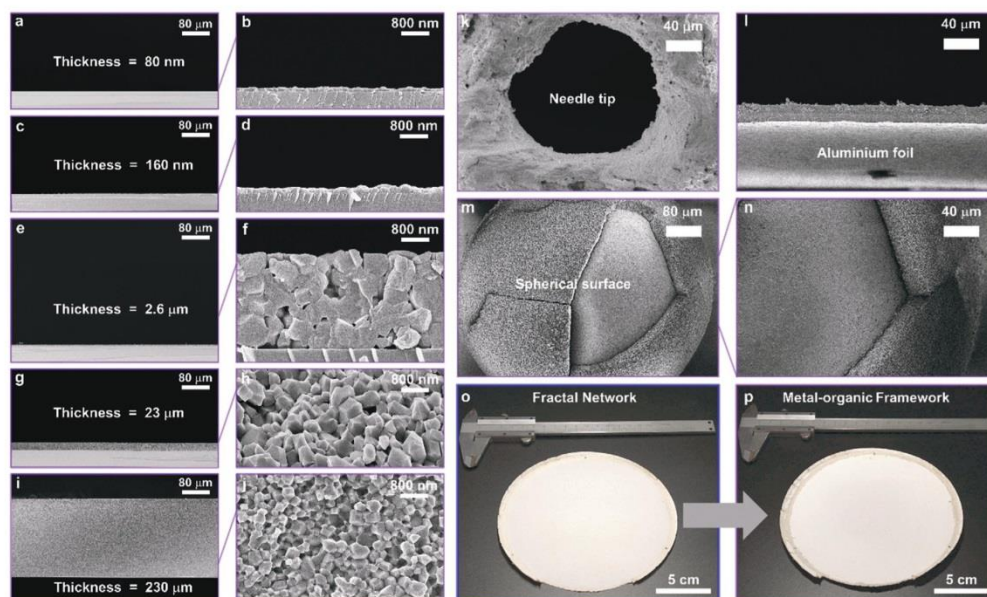




**Figure 2.** Tuning the extrinsic porosity of hierarchical ZIF-8 films. Cross-sectional SEM images of ZIF-8 films with: a) 66% extrinsic porosity ( $T_R = 90$  °C); b) 43% extrinsic porosity ( $T_R = 100$  °C); c) 11% extrinsic porosity ( $T_R = 120$  °C); d) 4% extrinsic porosity ( $T_R = 150$  °C). e) Scheme of grain coalescence of ZIF-8 crystals based on ZIF-8 obtained at 90 and 150 °C (f,g, respectively). h) Correlation between the extrinsic ZIF-8 porosity and the reaction temperature. i) XRD patterns of a ZnO FNN (dark blue line) and the resulting ZIF-8 films as a function of the conversion temperature.

temperature ( $T_R$ ). **Figure 2a–d** shows ZIF-8 films obtained at 90–150 °C. At  $T_R = 90$  °C, the thickness of the ZnO FNN precursor was maintained in the MOF film, and an extrinsic porosity of 66% was measured (**Figure 2a**, **Figures S14 c–d**, **S15** and **Table S1**, Supporting Information). The increase in solid fraction (SF) from the precursor ZnO FNN (SF = 2%) to the ZIF-8 film (SF = 34%) matches well with the 17 folds' theoretical volume expansion from ZnO (wurtzite) to ZIF-8.<sup>[17]</sup> The compaction of the MOF films with increasing reaction temperatures was attributed to the coalescence of the MOF grains (**Figure 2e**). Increasing  $T_R$  from 90 to 100, 110, 120, and 150 °C, induced a progressive compaction and a reduction in the extrinsic porosity from 66% to 43%, 27%, 11%, and 4%, respectively (**Figure 2a–d**, **f–g**, **Figures S15–19** and **Table S1**, Supporting Information). The extrinsic porosity decreases linearly with  $T_R$  below 120 °C (**Figure 2h**), with high reproducibility (**Table S1**, Supporting Information). Full ZnO conversion was observed irrespective of  $T_R$  (**Figure 2i**, **Figure S10**, Supporting Information).

The diffraction plot after 10 min conversion (flame-made ZnO FNN in presence of 2-MIM at 90 °C) shows a full conversion. By increasing the reaction time (18 h) of ZnO in presence of 2-MIM at 90 °C we did not observe in any further densification of the ZIF-8 films. Thus, the here reported nanoparticle network of 20 nm ZnO showed a similar reaction kinetics to the previously reported dense ZnO 10 nm films (i.e., 10–30 min vapor-phase reaction for a full conversion into crystalline ZIF-8, sod).<sup>[17]</sup> In the reactor, we added an amount of ligand sufficient to maintain its saturation pressure at all temperatures for the ZnO conversion to ZIF-8 (see Supporting Information). To examine the effect of the saturation pressure, we decreased the amount of 2-MIM from 100 mg to 2 mg for the 150 °C conversion temperature. By our calculation, the pressure with 2 mg ( $P_{2\text{mg}@150} = 1070.90$  Pa) is 42% the saturation pressure at 150 °C. With  $P_{2\text{mg}@150}$ , after 18 h reaction time at 150 °C, we observed only a partial conversion of ZnO to ZIF-8 (**Figure S32**, Supporting Information). Our experiments suggest that the conversion of ZnO to ZIF-8 can be enhanced when the



**Figure 3.** Controlling the ZIF-8 film thickness range and versatile coatings. a–j) Representative cross-sectional scanning electron microscope images of ZIF-8 films with an extrinsic porosity of 4%, obtained by conversion of ZnO FNNs at 150 °C. The ZIF-8 film thickness (80 nm to 230 μm) was controlled by tuning the amount of deposited ZnO. k) SEM image of a ZIF-8 channel prepared using a template. l–n) Cross-sectional SEM images of a ZIF-8-coated aluminum foil and sphere. o, p) Images of a ZnO precursor film deposited on a 177 cm<sup>2</sup> glass fiber, before and after conversion to ZIF-8.

pressure of the ligand in the gas phase is equal, or higher, to its saturation pressure.

FNNs afford the fabrication of nanometer- to millimeter-thick MOF films over areas >100 cm<sup>2</sup>. **Figure 3** shows crack-free ZIF-8 films with a thickness ranging from 80 to 0.23 mm (Figure 3a–j, Figure S20, Supporting Information). Thermogravimetric and XRD analysis confirmed the complete conversion of the ZnO precursor (Figures S21–S22, Supporting Information). MOF coatings were fabricated on a needle ( $\varnothing = 550 \mu\text{m}$ ), a ceramic milling ball ( $\varnothing = 1 \text{ mm}$ ), and flexible aluminum foils (Figure 3k–n, Figure S23, Supporting Information). The scalability of the method was illustrated by coating a 177 cm<sup>2</sup> area with ZIF-8 (Figure 3o, p).

#### 4. Self-Supporting MOF Membranes as Battery Separators

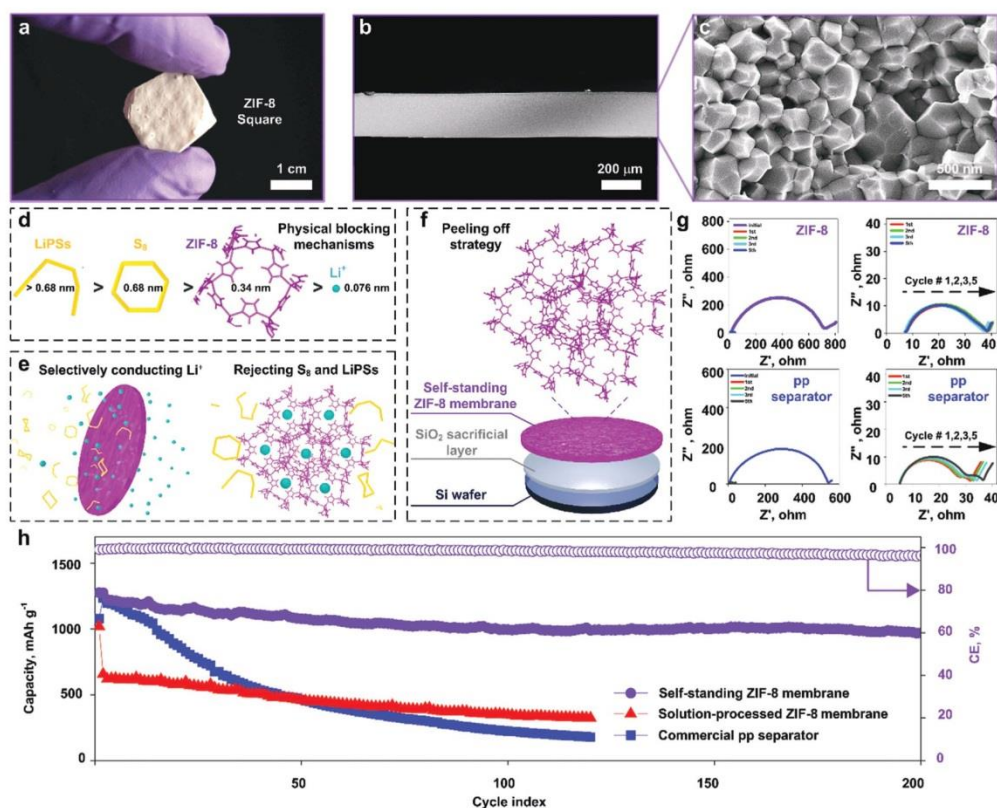
Typically, binderless MOF films are fragile and require specialized protocols to be transferred.<sup>[18]</sup> To fabricate robust, self-supporting MOF membranes, the ZnO FNN precursor was deposited on top of a sacrificial SiO<sub>2</sub> FNN (Figure S24, Supporting Information). As the SiO<sub>2</sub> particles are kept together only by weak van der Waals forces,<sup>[25]</sup> minimal mechanical stress is required for the lift-off of the MOF membrane. This approach could be used to fabricate self-supporting ZIF-8 membranes with a thickness ranging from 12 to 230 μm (Figure 4a–c, Figure S24b–c, g–i, Supporting Information). Due to the ZnO FNN deposition rate

(120 min for a 0.66 mm thick FNN on 177 cm<sup>2</sup>), we limited the precursor thickness. However, thicker MOF-based components could be prepared at higher deposition rates.<sup>[21]</sup>

MOFs membranes can display selective ion conductivity.<sup>[26]</sup> This property is highly desirable to realize the potential of Li-S batteries, since Li<sup>+</sup> should diffuse through the separator while the migration of Li-polysulfides (LiPSs) should be prevented. Based on its 0.34 nm pore aperture, ZIF-8 (sodalite topology) should be able to discriminate between Li<sup>+</sup> (0.076 nm) and long-chain LiPSs (>0.68 nm) (Figure 4d, e), even when taking into account the framework flexibility.<sup>[27]</sup> Existing MOF fabrication protocols did not yield a crack-free membrane.<sup>[28]</sup> Therefore, self-supporting ZIF-8 membranes with <4% extrinsic porosity and a thickness similar to that of commercial polypropylene (pp) separators (23 μm) were fabricated using our approach and tested as molecular sieve components (Figure 4f, Figure S25, Supporting Information).

To investigate the ability of the ZIF-8 separator to discriminate between Li<sup>+</sup> on the one hand and S<sub>8</sub> and LiPSs on the other, electrochemical impedance spectroscopy (EIS) measurements were performed (Figure 4g, Figure S28, Supporting Information). To compare with commercially available pp separators, a set of control measurements was performed as well. The near-identical impedance (Figure 4g, Figure S28, Supporting Information) of the cells with ZIF-8 and commercial separators indicates that the MOF membrane thickness and pore size do not





**Figure 4.** Self-supporting ZIF-8 membranes as battery separators. a–c) Optical and cross-sectional SEM images of a self-supporting square ZIF-8 membrane. d,e) ZIF-8 is expected to discriminate Li<sup>+</sup> and Li-polysulfides based on their size. f) The peeling off strategy for the preparation of the self-supporting ZIF-8 separator (1.9 cm in diameter and  $\approx 23 \mu\text{m}$  in thickness). g) Ionic conductivity (Li<sup>+</sup>) and blocking effect for LiPSs characterized by electrochemical impedance spectroscopy (EIS). h) Efficient LiPS molecular sieving demonstrated by the improved cycling performance when the ZIF-8 separator is used.

inhibit Li<sup>+</sup> transfer, in agreement with previous reports.<sup>[29]</sup> Additionally, cyclic voltammetry measurements (Figure S27, Supporting Information) suggest that ZIF-8 does not affect the redox reaction in the model Li-S battery in the voltage window of 1.5–2.8 V versus Li/Li<sup>+</sup>. The slight variation of the initial impedance between the ZIF-8 and control cells (Figure 4g, first and second row on the left) might be attributed to the incomplete wetting of the MOF membrane during the fabrication of the cell.<sup>[12,30]</sup> The EIS data for the ZIF-8 cell (Figure 4g, top-right) reveal that the MOF membrane successfully blocks the migration of LiPSs, thus preventing the shuttle effect. In contrast, the control cells showed a large impedance variation within the first five cycles (Figure 4g, bottom-right). Furthermore, the EIS data of the control cells show two semicircles in the high- and medium-frequency regions, as well as an increment of both semicircles from the 1<sup>st</sup> to the 5<sup>th</sup> cycle (Figure 4g, bottom-right). These observations are attributed to the undesirable deposition of Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub> on the anode and the

growth of an additional solid-electrolyte interface, respectively, and indicate a severe shuttle effect.

To further evaluate the performance of self-supporting ZIF-8 membranes obtained through FNN conversion, control cells were constructed with glass-fiber or commercial pp separators coated with ZIF-8 through a solvothermal protocol (Figure 4h, Figure S26, Supporting Information). The cells with self-supporting ZIF-8 membranes (Figure 4h, violet circles) delivered a high initial capacity of  $1276 \text{ mAhg}^{-1}$  at a discharge rate of 0.4 C and exhibited an improved cyclability with a small capacity fading rate of 0.12% per cycle and high Coulombic efficiency of above 96.5% for over 200 cycles. In contrast, the cells using the separators coated solvothermally with ZIF-8 (Figure 4h, red triangles and blue cubes) suffered from a drastic capacity degradation within only a few cycles. In addition, the cells using the self-standing ZIF-8 membranes were further tested for 200 cycles at a doubled discharge rate of 0.8 C (i.e., a doubled current

density). This higher rate resulted in a reduced initial capacity of 829 mAh g<sup>-1</sup> and a retention of 62.1% (Figure S33, Supporting Information), in line with the literature.<sup>[31]</sup> This performance demonstrates an interesting cycling performance of our self-standing ZIF-8 membranes also at higher current density. Notably, our self-standing ZIF-8 separators showed among the best sets of properties when compared to other MOF-based separators<sup>[32,33]</sup> (Table S2, Supporting Information). The densified monolithic morphology and crystallinity of the self-standing ZIF-8 separators are well-preserved after 200 charging/discharging cycles at 0.4 C (Figure S34, Supporting Information), indicating mechanical and chemical stability over the battery test.

## 5. Conclusion

We presented a flexible and scalable strategy for the fabrication of MOF films and self-supporting membranes with tunable hierarchical porosity via vapor phase conversion of metal oxide nanoparticle networks. With this protocol we fabricated pure MOF films with tunable extrinsic interparticle porosity, and controllable thickness in the 80 nm to 230 µm range for areas >100 cm<sup>2</sup>. We determined that for thicknesses in the 12–230 µm range, self-supporting membranes can be prepared. A 23 µm thick ZIF-8 self-standing membrane fabricated via this approach was used as battery separator, and it acted as an effective perm-selective barrier capable of blocking the migration of polysulfide species while permitting Li<sup>+</sup> transport in Li-S batteries, thus resulting in a significantly improved battery cyclability.

## 6. Experimental Section

All chemicals were used without further purification unless otherwise noted. *m*-xylene (99.9%), 2-methylimidazole (99%), trimesic acid (95%), terephthalic acid (98%), and zinc acetate dihydrate (>98%) were purchased from Sigma-Aldrich. Zinc-naphthenate (Zn 10%), copper-naphthenate (Cu 8%), and iron-naphthenate (Fe 6%) were purchased from Strem. Lithium foil (99.9%), SuperP carbon black, and polyvinylidene fluoride (PVDF) binder (99.5%) were purchased from MTI Corporation. Sulfur (99.98%), 1-methyl-2-pyrrolidinone (NMP) solvent (anhydrous 99.5%), 1,3-dioxolane (DOL 99.5%), 1,2-dimethoxyethane (DME 99.5%), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.9%) were purchased from Sigma-Aldrich. Lithium nitrate (LiNO<sub>3</sub> anhydrous 99.98%) was purchased from Alfa Aesar.

A flame spray pyrolysis (FSP) system (see Figure S29, Supporting Information) with ceramic precursors was used for the preparation of the ZnO FNNs. Liquid precursor solutions of zinc-naphthenate in *m*-xylene with a total metal ion concentration of 0.1, 0.2, and 0.3 mol L<sup>-1</sup> were supplied to the FSP nozzle and combusted to produce ZnO nanoparticle-loaded aerosols with customized particle size distributions, as previously discussed.<sup>[23]</sup> Crystalline ZnO FNNs with tunable porosity were synthesized by the self-assembly of the ZnO aerosols on a variety of substrates placed at a specific height above the burner (HAB). Increasing the HAB from 6 to 20 cm, the nanoparticle network porosity increased from 11% to 98%, respectively. The thickness of the resulting nanoparticle network was linearly controlled by the exposure time of the substrate to the nanoparticle aerosols.

ZnO FNNs were deposited at an HAB of 45 cm on circular glass fiber filters of 15 cm in diameter with the help of a vacuum pump. The coated glass fiber filters were placed in a squared stainless-steel reaction chamber (16.5 × 16.5 × 2 cm of internal space, wall thickness: 1 cm, with a stainless steel cover lid of 20 × 20 × 1 cm), with the ZnO FNNs facing up (see Figure

S30, Supporting Information). The chamber was pre-filled with 15 g of 2-MIM placed at the bottom of the internal space, leaving the middle area empty. The membrane was placed over a wire net (15 × 15 cm), in order to leave about 1 cm of space between the membrane and the bottom of the chamber, avoiding direct contact with the ligand powder. The chamber was sealed with a little amount of vacuum grease, to avoid leakage of ligand vapors, then placed in an oven at 120 °C for 18 h. After the reaction time the chamber was left to cool at room temperature naturally before opening.

For the synthesis of ZIF-8 monoliths, first, a glass vial containing 2-methylimidazole (2-MIM) solid crystals was placed into a Teflon lined stainless steel autoclave vial (see Figure S31, Supporting Information) as the vapor source. Thereafter, the ZnO FNNs were placed on a sample holder in the same autoclave. The autoclave was sealed and heated up to varied temperatures (90–150 °C) at a rate of 10 °C min<sup>-1</sup> using a gravity convection oven and kept for 18 h.

For the synthesis of reference ZIF-8 particles, zinc acetate dihydrate and 2-methylimidazole (2-MIM) were used without further purification in the experiments. The synthesis was performed with an excess amount of 2-MIM ligand and a minimal amount of water (molar ratio of Zinc acetate dihydrate:2-MIM:H<sub>2</sub>O = 1:8:600); 1 mmol of zinc acetate dihydrate and 8 mmol of 2-MIM were dissolved separately in 300 mmol of water. The zinc acetate solution was added to the 2-MIM solution while being stirred with a magnetic stirrer for 2 h at room temperature. White powders were collected by centrifugation for 10 min, washing twice with ethanol and drying overnight in the oven at 60 °C.

Synchrotron SAXS experiments were conducted in a capillary at the AustroSAXS beamline of Elettra Synchrotron (Trieste, IT). The starting temperature was 25 °C, and the heating rate was 10 °C min<sup>-1</sup>, and the temperature reached 120 °C in approximately 9.5 min.

All XRD patterns were collected using a Bruker system (XRD, D2 Phaser, USA) equipped with Cu Kα radiation (1.54059 Å).

N<sub>2</sub> adsorption isotherms of the degassed specimens were recorded at liquid nitrogen temperature using a Tristar II (Micromeritics, USA). The Brunauer-Emmett-Teller model was applied to determine the specific surface area in the pressure range of *p/p*<sub>0</sub> between 0.001 and 0.05. The converted ZIF-8 MOF films were activated by heat treatment at 150 °C for 2 h prior to the tests.

FTIR spectra were recorded utilizing Bruker ALPHA II FTIR Spectrometer with the PLATINUM ATR module from 4000 to 400 cm<sup>-1</sup>.

All SEM images were collected using a Zeiss Ultraplus (FESEM) at 3 kV. All samples were coated with ≈2 nm Pt before the analysis. HRTEM and HAADF-STEM were carried out using a JEOL 2100F FEGTEM at 200 kV.

Model of cathode material for Li-S battery were prepared as follows. Elemental sulfur was first mixed with SuperP carbon black powders. The mixture was ground in a corundum mortar for 20 min followed by heating at 155 °C for 2 h in a sealed glass vial. After cooling to room temperature, it was mixed with PVDF in NMP solvent to make a slurry, where the ratio of sulfur, SuperP, and PVDF was 70:20:10 by weight. The slurry was stirred overnight and cast by doctor blading on aluminum (Al) foil current collectors (MTI Corp.). These cathodes were dried in a vacuum oven at 60 °C overnight. Battery assembly: 2032-type coin cells were assembled in an argon-filled glovebox. The prepared cathodes were punched into small discs with a diameter of 15 mm. A typical areal mass loading of the active material in cathode was ≈2.5 mg cm<sup>-2</sup>. Lithium metal foils (diameter/thickness: 16 mm/0.6 mm) were used as the anode. Celgard 2400 (pore size: 0.043 µm) was used as a separator. The electrolyte contained 1.0 M LiTFSI and 0.1 M LiNO<sub>3</sub> in a mixture of DME and DOL (1:1, vol./vol.). The galvanostatic discharge/charge measurements were conducted on a NEWARE BTS3000 battery test system. The cyclic voltammogram and EIS were carried out using a BioLogic VMP3 multi-channel potentiostat workstation. All electrochemical measurements were carried out at 20 °C.

Fractal analysis has been carried out via an image-processing software named FracLac<sup>[34]</sup> following the same procedure previously reported.<sup>[19,35]</sup> In brief, the fractal dimension is evaluated by the slope of a log(*N*) versus log(*ε*), where *N* is the number of pixels of sticks (foreground pixels) and *ε* is the scaling factor. While the lacunarity, a fractal parameter which takes into account the heterogeneity of the system, is calculated



via a series of grids with a decreasing size of the box,  $\epsilon$ , and counting the foreground pixels. For each grid of dimension  $\epsilon$ , the standard deviation,  $\sigma$ , and the mean,  $\mu$ , of the pixel per box are evaluated. The lacunarity for each grid is then computed as  $\lambda = (\sigma/\mu)^2$  and the average lacunarity is then given by:

$$\bar{\lambda} = \frac{1}{n} \sum_i \left( \frac{\sigma_i}{\mu_i} \right) + 1 \quad (1)$$

where the summation is over all the grids with dimension  $\epsilon$ . Note that this equation has a "+1" added for completeness to take into account the eventuality of a total homogeneous (no variation in the pixel distribution) image.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

extrinsic porosity, metal-organic frameworks, molecular sieving, 3D structuring

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## Supporting Information

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### Hierarchical Metal-Organic Framework Films with Controllable Meso/Macroporosity

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## Supporting Information

**Three-Dimensional Structuring of Hierarchical Metal-Organic Frameworks Monoliths**

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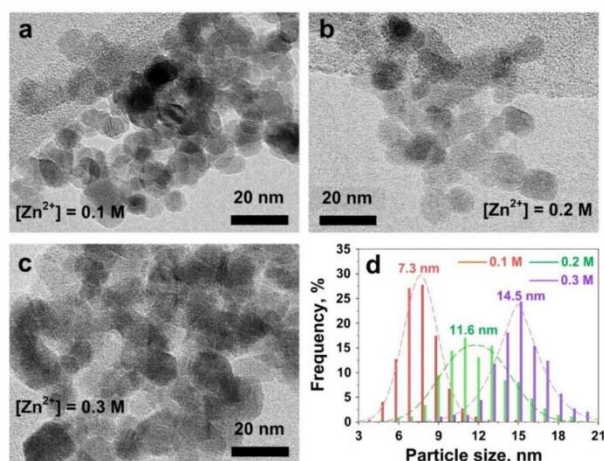
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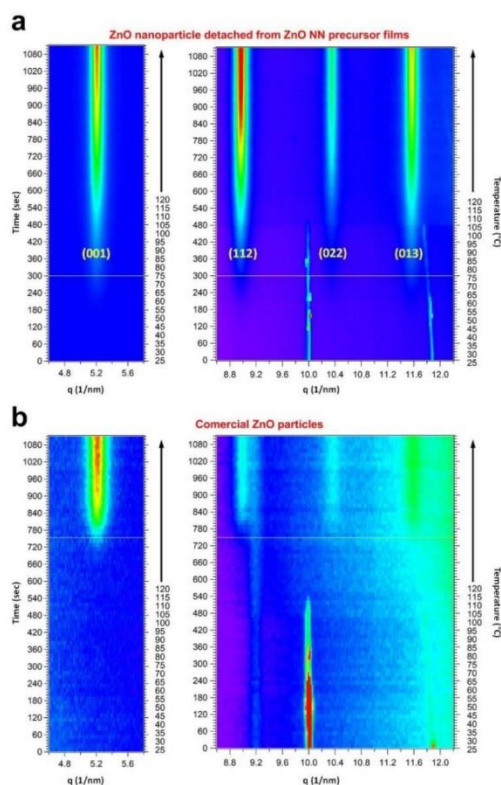
Engineering the size of the ceramic nanoparticle precursor was achieved by controlling the metal precursor concentration supplied to the flame spray pyrolysis burner. The injection of a solution with lower concentrations of the metal precursor leads to aerosols composed by particles with smaller size. Here, the metal precursor concentration was varied from 0.1 to 0.3 mol L<sup>-1</sup>. Transmission electron microscopy (TEM) analysis was carried out by collection of the ZnO nanoparticles from the obtained nanoparticle networks (Figure S1a-c). Representative particle size distributions (Figure S1d) were calculated by counting 300 ZnO nanoparticles for all different precursor concentrations showing a good control over the particle size of the ceramic precursor. This control over size is crucial to achieve full conversion from ZnO to ZIF-8 by gas phase; indeed, this reaction is generally limited to a thin layer of 10-15 nanometres from the surface of the ceramic particles.<sup>[1, 2]</sup> A metal precursor concentration of 0.3 mol L<sup>-1</sup> was selected as it afforded: 1) particles smaller than 20 nm (whereas the limit for gas phase conversion is *ca* 15 nm),<sup>[1, 2]</sup> and 2) the highest concentration of nanoparticle in the aerosol. Thus the nanoparticle network growth rate was optimized.



**Figure S1** Engineering of the precursor ceramic particle size. **a-c**, Representative TEM images of engineered ZnO nanoparticles made by flame spray pyrolysis with liquid precursor concentrations of 0.1, 0.2 and 0.3 mol.L<sup>-1</sup>. **d**, Particle size distributions of the flame-made precursor ZnO nanoparticles with liquid precursor concentrations of 0.1, 0.2 and 0.3 mol.L<sup>-1</sup>.

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The gas-phase conversion kinetics of the engineered flame-made ZnO nanoparticles, obtained with a liquid precursor concentration of  $0.3 \text{ mol.L}^{-1}$  (*vide supra*), to ZIF-8 was monitored via *in situ* synchrotron small-angle X-ray scattering (SAXS). Figure S2 shows the first 18 minutes of reaction of ZnO with 2-MIM vapors from room temperature up to maximum  $120^\circ\text{C}$  (whereas the melting point of 2-MIM is *ca*  $142^\circ\text{C}$ ), for both flame-made ZnO nanoparticles collected from the ZnO nanoparticle networks and for commercial ZnO particles. The appearance of characteristic peaks of ZIF-8 lattice plane (001) in SAXS (Figure S2a, left), and lattice plane (112), (022) as well as (013) in wide-angle X-ray scattering (WAXS) (Figure S2a, right) indicates that the flame-made ZnO nanoparticles (collected from the FNNs) react with 2-MIM to produce ZIF-8 at *ca*  $75^\circ\text{C}$  after *ca* 5 min, while for the commercial ZnO powder the ZIF-8 characteristic peaks started being observed only at *ca* 12.5 min after reaching the maximum temperature (Figure S2b). The peaks observed at the beginning of the reaction at  $q = 10$  and  $12 \text{ 1/nm}$  correspond to those of the crystalline 2-MIM powder ligand. These findings reveal that the engineered flame-made ZnO nanoparticles are highly reactive precursors for MOF conversion.

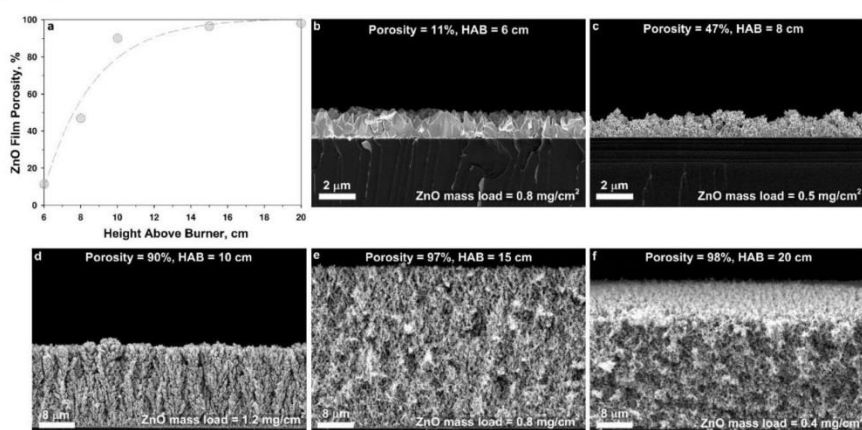


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**Figure S2** *In situ* synchrotron SAXS and WAXS monitoring of the reaction kinetics of the flame-made ZnO nanoparticles with 2-MIM vapours. *In situ* monitoring of the conversion of (a) flame-made ZnO nanoparticles detached from ZnO FNN precursor films and (b) commercial ZnO particles.

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In addition to the particle size, engineering the extrinsic porosity of the fractal nanoparticle networks (FNNs) is the key for successful conversion of the ceramic precursor particles into a monolithic MOF film. This is particularly important as during ceramic to MOF conversion the solid fraction volume of the film increases significantly (e.g. 17 times from ZnO to ZIF-8)<sup>[2]</sup>, thus, a sufficient extrinsic porosity of the precursor ceramic film is required to avoid strain and ensure continuous exposure of the ceramic precursor to the ligand vapours. To investigate the effect of the FNN extrinsic porosity on the converted MOF, ZnO films with porosity ranging from 11% to 98%, here named extrinsic porosity, were fabricated by changing the height above the flames spray pyrolysis burner (HAB) at which the substrates were placed, as described elsewhere.<sup>[3]</sup>

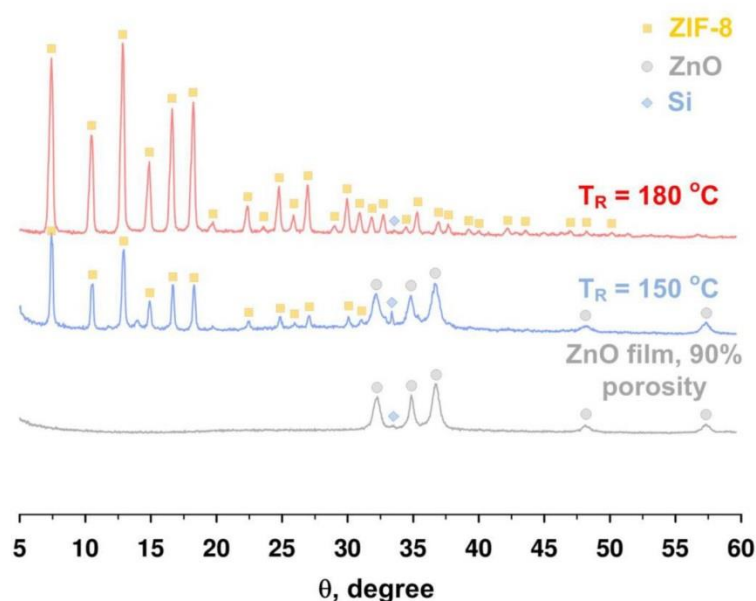


**Figure S3 Engineering of the extrinsic porosity of the fractal precursor ZnO nanoparticle networks (FNNs).** **a**, Extrinsic porosity of ZnO FNNs as a function of the height above the burner (HAB). **b-f**, Cross-sectional SEM images of ZnO FNNs with engineered extrinsic porosities from 11 - 98% and various ZnO mass loading. It should be noted that the thickness of the 97% porous FNN is higher than that of the 98% one, due to the doubled mass loading comparing to the former. All samples were coated with a thin layer of Pt (*ca* 2 nm) to facilitate imaging.



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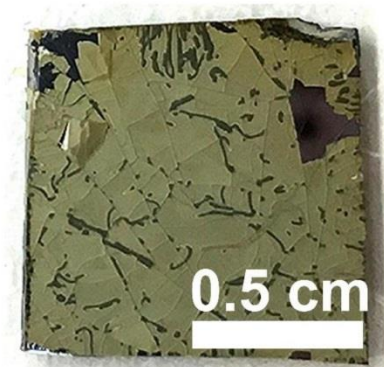
Characterization of the converted ZnO FNNs (90% extrinsic porosity) into ZIF-8 films. XRD measurements were performed on the ZnO FNN before and after reaction with the 2-MIM vapour at 150 °C and 180 °C. While some of the ZIF-8 characteristic peaks were detected at 150 °C, the reaction was still not completed upon 18 h at this temperature. Further increasing the temperature to 180 °C and reacting for 18 h resulted in disappearance of the ZnO characteristic peaks and in rise of the ZIF-8 characteristic reflections. However, cracks were observed as shown in Figure S5.



**Figure S4 XRD patterns of the 90% porous ZnO FNN before and after exposure to 2-MIM vapour at 150 and 180 °C.** XRD patterns of ZnO FNN with 90% extrinsic porosity before (grey line) and after conversion at 150 °C (light blue line) and 180 °C (red line).

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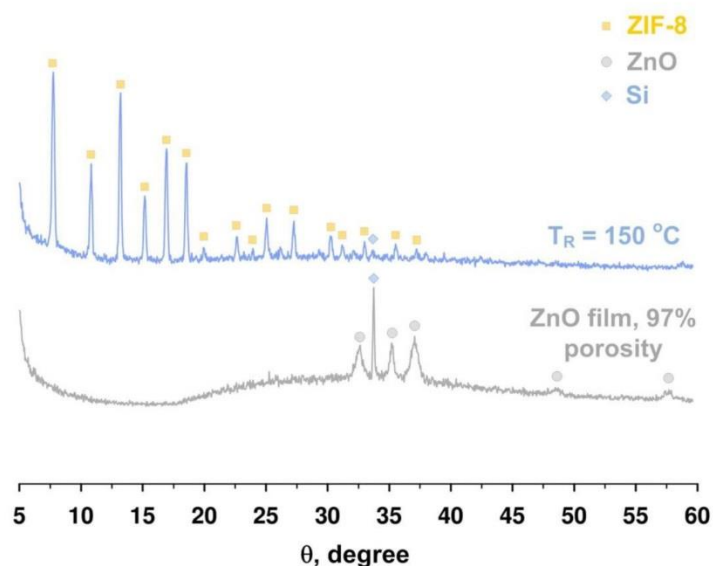
Optical image of the 90% porous ZnO FNN converted to ZIF-8 at 180 °C. Upon the reaction, formation of cracks and partial delamination of the resulting film is observed. It can be attributed to the insufficient void space that cannot accommodate the 17-fold expansion of the crystal lattice from ZnO to ZIF-8.<sup>[2]</sup> This experimental observation is in line with our calculation (see Supplementary Calculation Equation 1) that indicates a minimum required extrinsic porosity of 94.12% for full conversion of ZnO nanoparticle network to ZIF-8 monoliths.



**Figure S5** Optical image of the 90% porous ZnO FNN converted to ZIF-8 at 180 °C. The formation of cracks and partial delamination of the resulting film is observed at this lower porosity.

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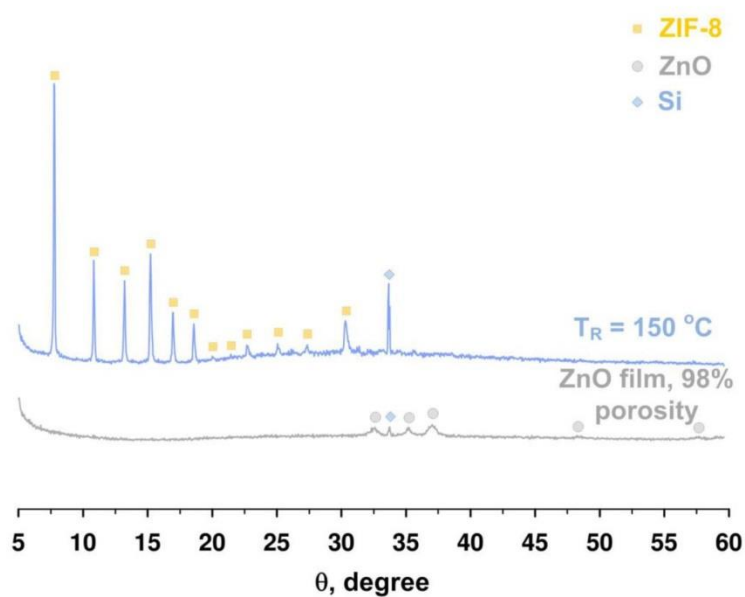
XRD measurements were performed on the ZnO FNN (97% extrinsic porosity) before and after reaction with the 2-MIM vapour at 150 °C for 18 h. The typical diffraction peaks of the wurtzite (ZnO)<sup>[4]</sup> (Figure S6 grey line) disappeared after reaction with 2-MIM. After the reaction the typical diffraction pattern of ZIF-8 (Figure S6 blue line) was observed.<sup>[2]</sup>



**Figure S6 XRD patterns of the 97% porous ZnO FNN before and after exposure to 2-MIM vapour at 150 °C.** The XRD diffraction patterns of the 97% ZnO FNN before (grey line) and after conversion at 150 °C (light blue) confirm the complete conversion.

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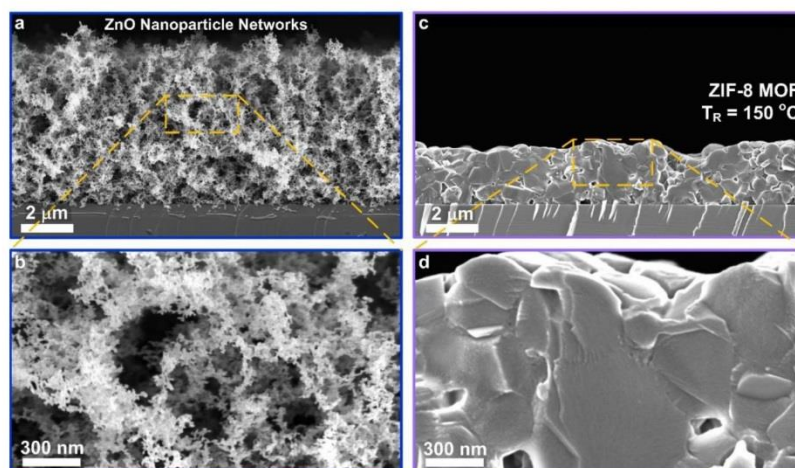
XRD measurements were performed on the ZnO FNN (98% extrinsic porosity) before and after reaction with the 2-MIM vapour at 150 °C for 18 h. The typical diffraction peaks of wurtzite (ZnO)<sup>[4]</sup> (Figure S7 grey line) disappeared after reaction with 2-MIM. After reaction, the typical diffraction pattern of ZIF-8<sup>[2]</sup> (Figure S7 blue line) was observed. In comparison to the XRD spectra of the MOFs converted from the 97% porous nanoparticle networks, a sharpening of the diffraction peaks was observed, indicating growth of larger MOF crystals.



**Figure S7 XRD patterns of the 98% porous ZnO FNN before and after exposure to 2-MIM vapour at 150 °C.** The XRD diffraction patterns of the 98% ZnO FNN before (grey line) and after conversion at 150 °C (light blue) confirm the complete conversion.

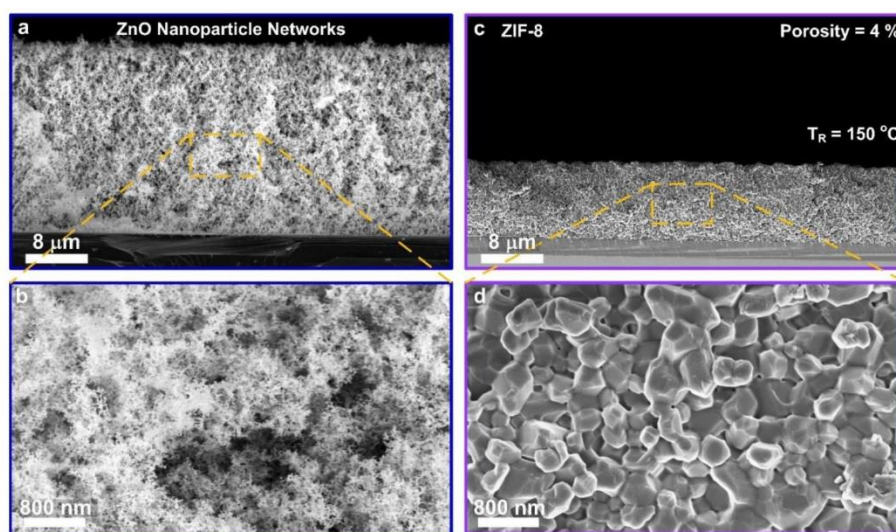
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Figure S8 shows the cross-sectional SEM images of a 98% porous ZnO FNN (Figure S8a, b) and the ZIF-8 monolithic film (Figure S8c, d) obtained through reaction with 2-MIM vapour at 150 °C for 18 hours. A film thickness contraction factor of *ca* 2.8 was observed with respect to the precursor film, resulting in a dense ZIF-8 monolithic structure with only *ca* 4 ± 2% extrinsic porosity.



**Figure S8 Morphological studies of the 98% porous ZnO FNN with a thickness of 7 μm converted into ZIF-8 at 150 °C.** **a**, Cross-sectional SEM image of a 7 μm thick precursor ZnO FNN and **(b)** the corresponding higher magnification image. **c**, Cross-sectional SEM image of the converted ZIF-8 film and **(d)** the corresponding higher magnification. All samples were coated with a thin layer of Pt (*ca* 2 nm) to avoid charging.

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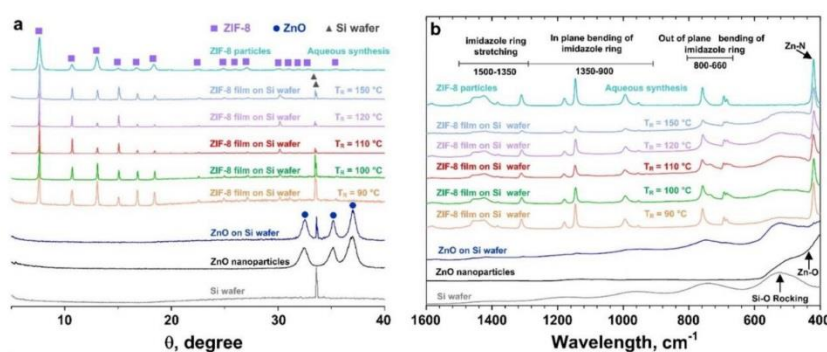


**Figure S9** Morphological studies of the 98% porous ZnO FNN with a thickness of 33  $\mu\text{m}$  converted into ZIF-8 at 150  $^{\circ}\text{C}$ . **a**, Cross-sectional SEM image of a 33  $\mu\text{m}$  thick precursor ZnO FNN and **(b)** the corresponding higher magnification image. **c**, Cross-sectional SEM image of the converted ZIF-8 film and **(d)** the corresponding higher magnification. All samples were coated with a thin layer of Pt (*ca* 2 nm) to avoid charging.



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To further verify the full conversion of the ceramic precursor and investigate the impact of reaction temperature on the conversion of the precursor ZnO FNN into ZIF-8 monoliths, a series of XRD and FTIR characterizations were performed and compared to ZIF-8 powders obtained by an established aqueous synthesis.<sup>[5]</sup> Notably and in line with the *in situ* synchrotron measurements (*vide supra*), all reaction temperatures from 90 to 150 °C resulted in the full conversion of the 98% porous ZnO nanoparticle networks into ZIF-8. The XRD characteristic peaks of wurtzite (ZnO)<sup>[4]</sup> of the FNNs (Figure S10a, dark blue line) matches well those of the ZnO nanoparticles (Figure 10a, black line). Upon reaction with 2-MIM, the ZnO lattice diffraction peaks were replaced by the characteristic peaks of the ZIF-8 (sodalite)<sup>[2]</sup> at all tested temperatures (Figure S10a, ZIF-8 on Si wafer at 90 – 150 °C) indicating full conversion of the precursor FNNs. Fourier-transform infrared spectroscopy (FTIR) measurements were carried out on the same set of samples. Both the ZnO FNN on Si wafer (Figure S10b, dark blue line) and the pure ZnO nanoparticles (Figure S10, black line) FTIR spectra show the characteristic bond of Zn-O stretching at 440 cm<sup>-1</sup>. Comparison of the FTIR spectra of the pure ZIF-8 particles made by aqueous synthesis (Figure S10b, dark cyan line) and the ZIF-8 monoliths obtained by conversion of the ZnO FNN at 90 – 150 °C (Figure S10, ZIF-8 films on Si wafer) confirms that pure ZIF-8 films were obtained. The observed characteristic modes at 1500 – 1350, 1350 – 900, 800 – 660 and 423 cm<sup>-1</sup> are corresponding to imidazole ring stretching, in plane bending of imidazole ring, out of plane bending of imidazole ring and Zn-N stretching, respectively. In the reacted samples, the Zn-O stretching at 440 cm<sup>-1</sup> of the FNN were completely replaced by the Zn-N stretching at 423 cm<sup>-1</sup>. To be noted, the broad peaks observed at *ca* 520 – 500 cm<sup>-1</sup> in the bare Si wafer and in all films on Si wafer are attributed to the Si-O rocking,<sup>[6]</sup> which is expected to arise from the thin SiO<sub>2</sub> layer on the Si-wafers.



**Figure S10** XRD and FTIR characterizations of the ZnO nanoparticle network converted into ZIF-8 as a function of the conversion temperature. **a**, XRD patterns of a bare Si wafer used as

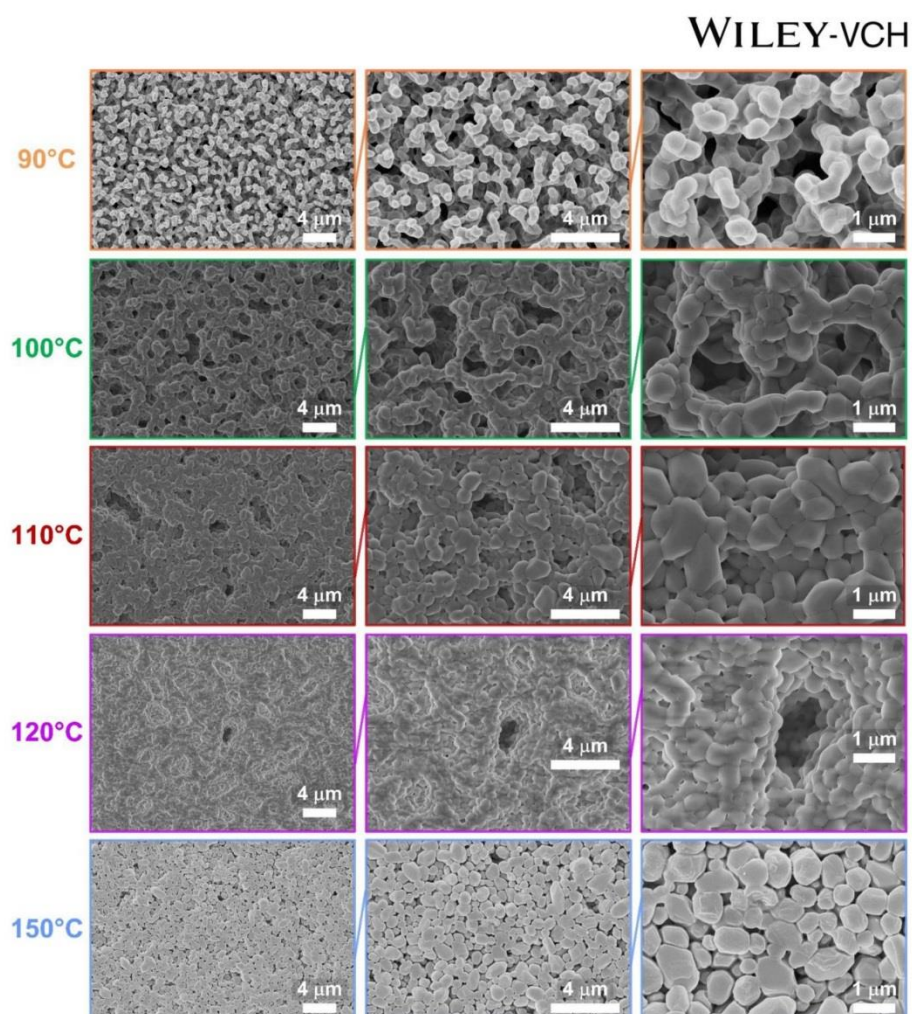
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substrate (grey line), pure flame-made ZnO nanoparticles (black line), ZnO nanoparticles on a Si wafer (dark blue line), the converted ZIF-8 monoliths at different conversion temperatures from 90 to 150 °C, and pure ZIF-8 particles obtained via the aqueous synthesis (dark cyan line).

**b**, FTIR spectra of a bare Si wafer used as substrate (grey line), pure flame-made ZnO nanoparticles (black line), ZnO nanoparticles on a Si wafer (dark blue line), the converted ZIF-8 monoliths at different conversion temperatures from 90 to 150 °C, and pure ZIF-8 particles obtained via the aqueous synthesis (dark cyan line).





**Figure S11** Top view SEM images of ZIF-8 films converted at varied temperatures. Colour codes: 90 °C is light orange, 100 °C is green, 110 °C is red, 120 °C is light purple and 150 °C is light blue.

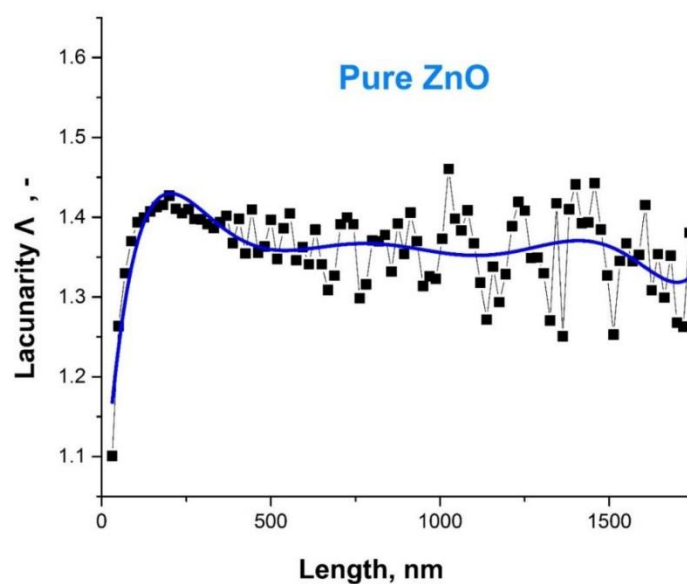
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The lacunarity, a fractal parameter, which takes into account the heterogeneity of the system, is calculated via a series of grids with a decreasing size of the box,  $\varepsilon$ , and counting the foreground pixels. For each grid of dimension  $\varepsilon$ , the standard deviation,  $\sigma$ , and the mean,  $\mu$ , of the pixel per box are evaluated. The lacunarity for each grid is then computed as  $\lambda = (\sigma/\mu)^2$  and the average lacunarity is then given by:

$$\bar{\lambda} = \frac{1}{n} \sum_i \left( \frac{\sigma_i}{\mu_i} \right)^2 + 1$$

where the summation is over all the grids with dimension  $\varepsilon$ . Note that this equation has a '+1' added for completeness to take into account the eventuality of a total homogeneous (no variation in the pixel distribution) image.

The lacunarity of pure ZnO (Figure S12) peaking at 100 – 400 nm is well in line with previous report.<sup>[7]</sup>



**Figure S12** The lacunarity evaluated by the pixel distribution of the images for pure ZnO nanoparticle network.

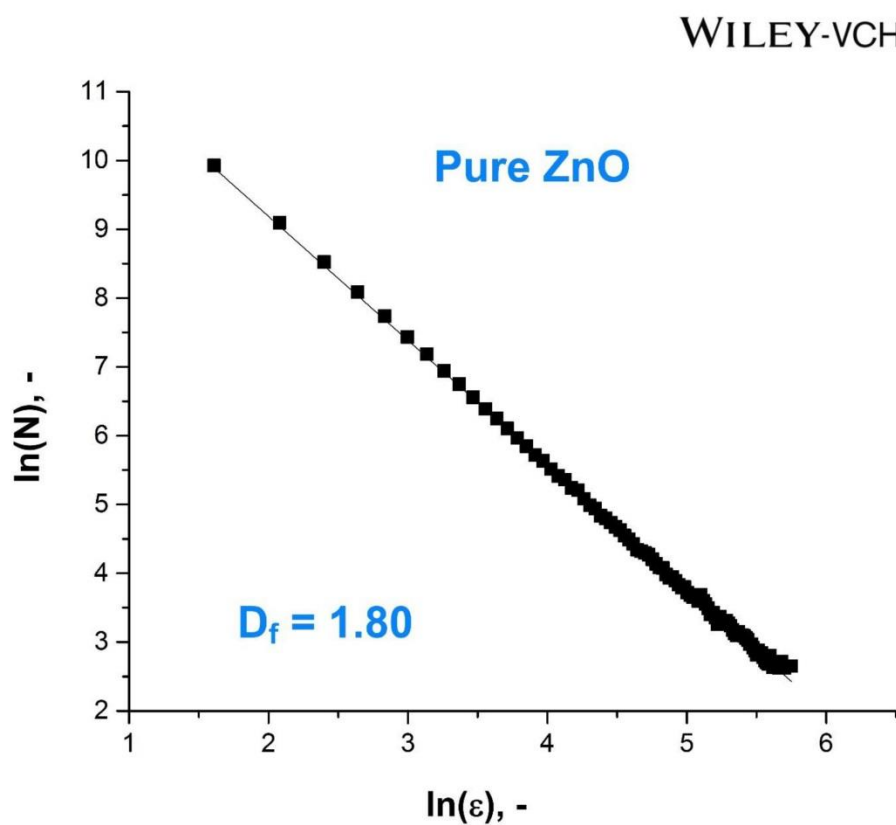
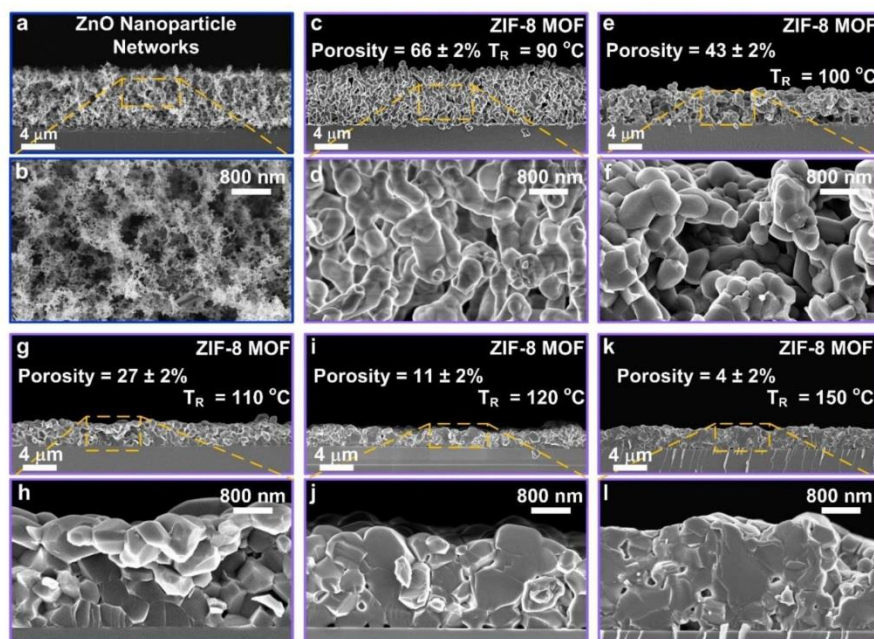


Figure S13 Fractal dimension of pure ZnO nanoparticle network.

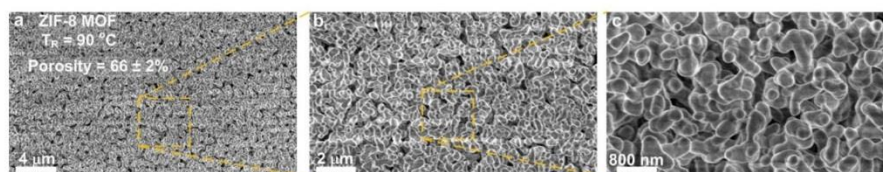
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**Figure S14 Engineering of the extrinsic porosity and hierarchy.** **a**, Cross-sectional SEM images of a 98% porous ZnO FNN precursor utilized for ZIF-8 monolith fabrication and **(b)** the corresponding high magnification SEM image of **a**. **c**, Cross-sectional SEM images of the ZIF-8 monolithic film with an extrinsic porosity of  $66 \pm 2\%$  obtained at  $90^\circ\text{C}$  and **(d)** the corresponding high magnification SEM image of **c**. **e**, Cross-sectional SEM images of the ZIF-8 monolithic film with an extrinsic porosity of  $43 \pm 2\%$  obtained at  $100^\circ\text{C}$  and **(f)** the corresponding high magnification SEM image of **e**. **g**, Cross-sectional SEM images of the ZIF-8 monolithic film an extrinsic porosity of  $27 \pm 2\%$  obtained at  $110^\circ\text{C}$  and **(h)** the corresponding high magnification SEM image of **g**. **i**, Cross-sectional SEM images of the ZIF-8 monolithic film with an extrinsic porosity of  $11 \pm 2\%$  obtained at  $120^\circ\text{C}$  and **(j)** the corresponding high magnification SEM image of **i**. **k**, Cross-sectional SEM images of the ZIF-8 monolithic film with an extrinsic porosity of  $4 \pm 2\%$  obtained at  $150^\circ\text{C}$  and **(l)** the corresponding high magnification SEM image of **k**. All samples were coated with a thin layer of Pt (*ca* 2 nm) to avoid charging.

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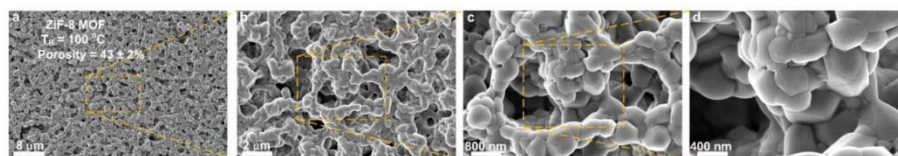
Representative top view SEM images of a ZIF-8 monolithic film with an extrinsic porosity of  $66 \pm 2\%$ , which are in line with the cross-sectional SEM images (**Figure 2**, Figure S15) obtained from the same film.



**Figure S15** Top view SEM images of ZIF-8 monolith with  $66 \pm 2\%$  extrinsic porosity. Increased magnifications are presented from **a** to **c**. No coating was deposited prior to SEM analysis.

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Representative top view SEM images of a ZIF-8 monolithic film with an extrinsic porosity of  $43 \pm 2\%$ , which are in line with the cross-sectional SEM images (**Figure 2**, Figure S16) obtained from the same film.

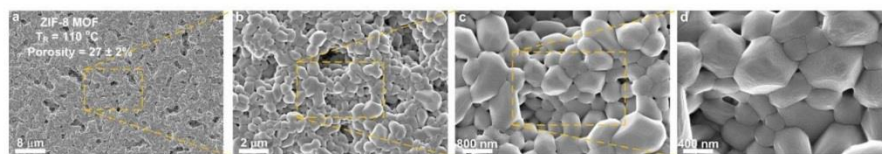


**Figure S16** Top view SEM images of ZIF-8 monolith with  $43 \pm 2\%$  extrinsic porosity. Increased magnifications are presented from **a** to **d**. All samples were coated with a thin layer of Pt (*ca* 2 nm) to avoid charging.



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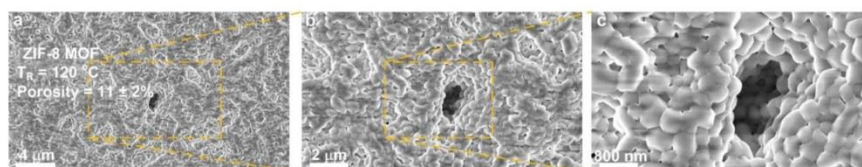
Representative top view SEM images of a ZIF-8 monolithic film with an extrinsic porosity of  $27 \pm 2\%$ , which are in line with the cross-sectional SEM images (Figure S17) obtained from the same film.



**Figure S17 Top view SEM images of ZIF-8 monolith with  $27 \pm 2\%$  extrinsic porosity.** Increased magnifications are presented from **a** to **d**. All samples were coated with a thin layer of Pt (*ca* 2 nm) to avoid charging.

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Representative top view SEM images of a ZIF-8 monolithic film with an extrinsic porosity of  $11 \pm 2\%$ , which are in line with the cross-sectional SEM images (**Figure 2**, Figure S18) obtained from the same film.

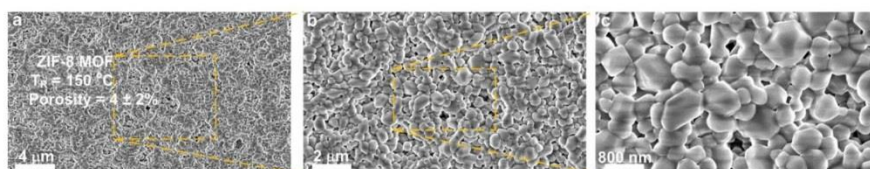


**Figure S18** Top view SEM images of ZIF-8 monolith with  $11 \pm 2\%$  extrinsic porosity. Increased magnifications are presented from **a** to **c**. No coating was deposited prior to SEM analysis.



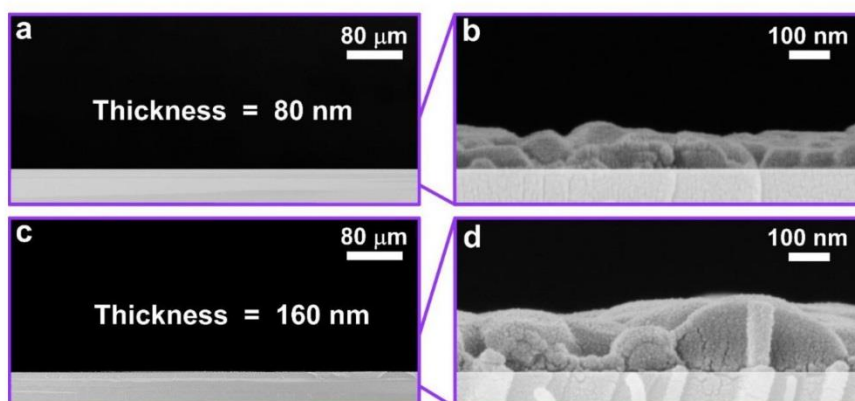
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Representative top view SEM images of a ZIF-8 monolithic film with an extrinsic porosity of  $4 \pm 2\%$ , which are in line with the cross-sectional SEM images (**Figure 2**, Figure S19) obtained from the same film.



**Figure S19** Top view SEM images of ZIF-8 monolith with  $4 \pm 2\%$  extrinsic porosity. Increased magnifications are presented from **a** to **c**. No coating was deposited prior to SEM analysis.

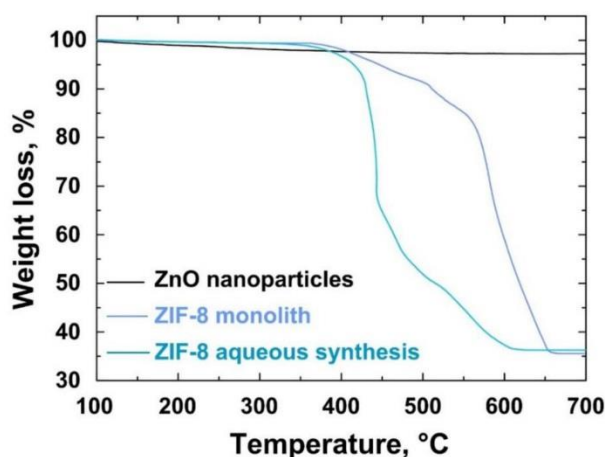
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**Figure S20** SEM images of 80 and 160 nm thick ZIF-8 films obtained by converting FNN. **a**, Cross-sectional SEM images of 80 nm thick ZIF-8 film and **(b)** the corresponding high magnification SEM image of **a**. **c**, Cross-sectional SEM images of 160 nm thick ZIF-8 film and **(d)** the corresponding high magnification SEM image of **c**. All samples were coated with a thin layer of Pt (*ca* 2 nm) to avoid charging.

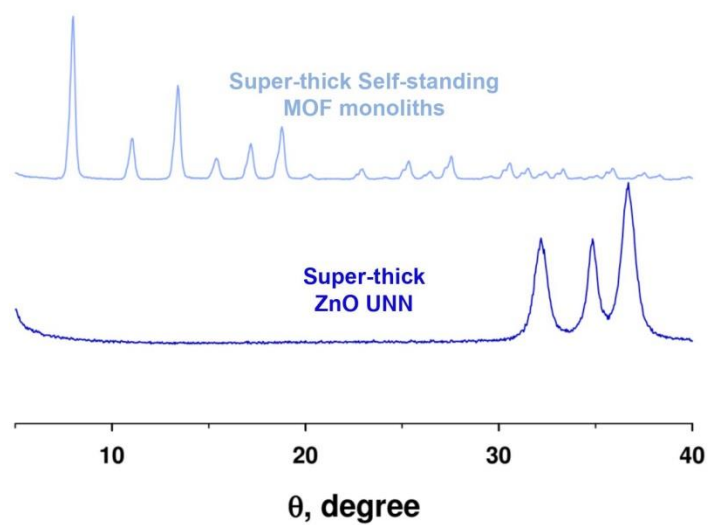
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TGA measurements were carried out with the pure flame-made ZnO nanoparticles, 230  $\mu\text{m}$ -thick ZIF-8 monoliths made by conversion of the ZnO FNN, and ZIF-8 particles prepared using the aqueous synthesis method. Both the ZIF-8 monoliths and ZIF-8 particles were degassed at 150  $^{\circ}\text{C}$  for 2 hours before TGA measurements. A 2.7% weight loss was observed with the pure ZnO nanoparticles up to 700  $^{\circ}\text{C}$ . This is attributed to the removal of absorbed moisture and trapped atmospheric components as previously reported.<sup>[8]</sup> For the MOFs, no obvious weight loss was observed from neither the ZIF-8 monoliths nor ZIF-8 particles up to 350  $^{\circ}\text{C}$  indicating a thermally stable ZIF-8 structure, in line with previous reports.<sup>[9]</sup> From 350 - 700  $^{\circ}\text{C}$ , a weight loss of 64.4% and 63.7% is observed for the ZIF-8 monoliths and ZIF-8 particles, respectively, which can be attributed to the re-conversion of the ZIF-8 into ZnO. Considering the possible experimental errors, these values are in good agreement. Additionally, given the theoretical weight loss of 64.2% from a pure ZIF-8 to a ZnO, these provide further evidence for the full conversion of the ZnO FNN into a ZIF-8 monolith of *ca* 230  $\mu\text{m}$  thick. The pure ZIF-8 structure of this 230  $\mu\text{m}$  thick ZIF-8 monolith was also confirmed by XRD measurements as shown in Figure S22.



**Figure S21 TGA characterization of the 230  $\mu\text{m}$  thick ZIF-8 monolith.** TGA curves of ZnO nanoparticles (black line), ZIF-8 monolith of *ca* 230  $\mu\text{m}$  thickness (blue line), and ZIF-8 particles made via aqueous synthesis (dark cyan line).

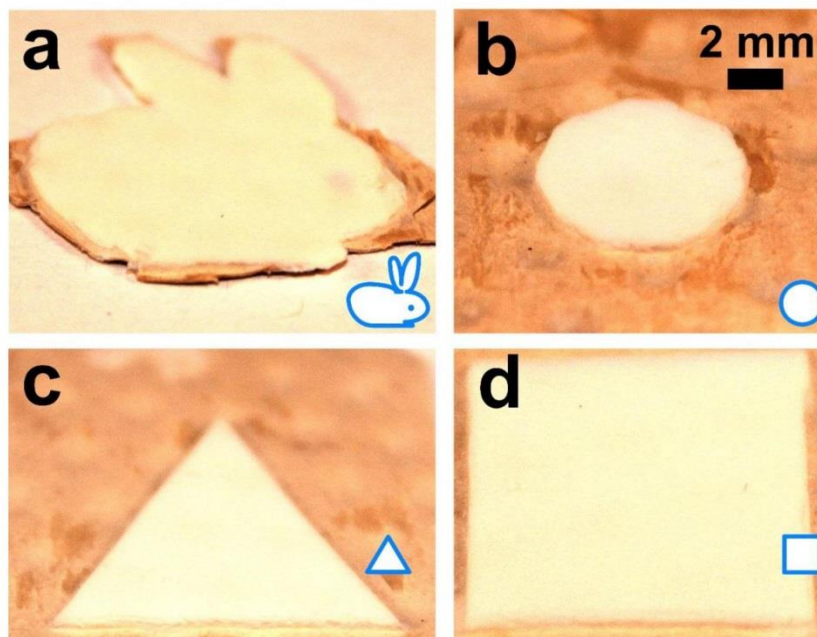
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**Figure S22** XRD analysis on the self-standing ZIF-8 monolith (*ca* 230  $\mu\text{m}$  thick) before and after conversion. XRD patterns of ZnO FNN precursor before conversion (dark blue line) and after conversion into ZIF-8 monolith (*ca* 230  $\mu\text{m}$  thick) (light blue line).

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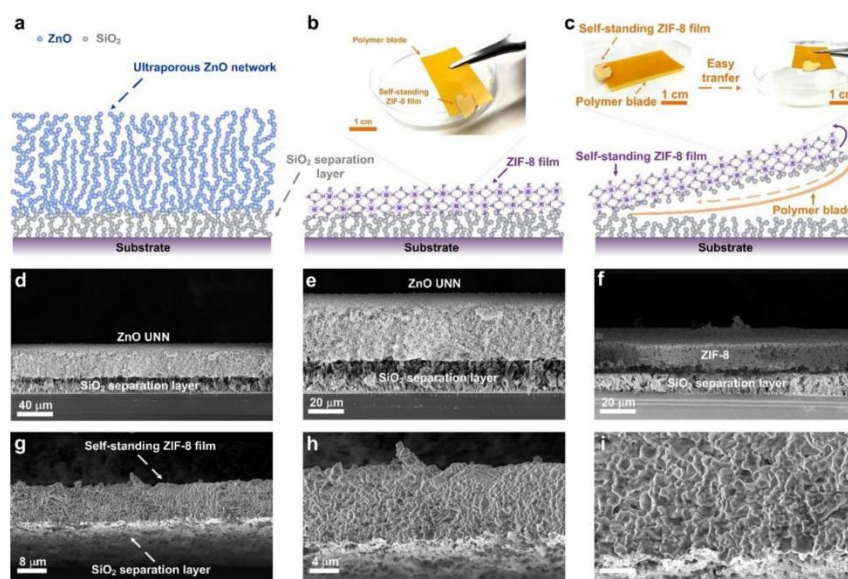
To demonstrate the designability of our proposed ceramic-to-MOF approach, ZnO FNNs with different designs have been prepared by either hand-drawing (Figure S23a-b) or introducing some existing templates (Figure S23c-d).



**Figure S23** Optical images of *ca* 0.66 mm thick ZnO FNNs with different designs. **a**, A FNN rabbit. **b**, A FNN disk. **c**, A FNN triangle. **d**, A FNN square.

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Fabrication of thinner monolithic self-standing MOF objects was achieved using our FNNs (Figure S24b, c, insets, self-standing ZIF-8 monolith of *ca* 12  $\mu\text{m}$  in thickness). To achieve this, a  $\text{SiO}_2$  FNN was used as the separation layer between the Si substrate and the ZnO FNN to facilitate the peeling off upon MOF conversion. More in detail, a double layer film consisting of a *ca* 30  $\mu\text{m}$  thick ZnO FNN on top of a *ca* 20  $\mu\text{m}$   $\text{SiO}_2$  FNN (Figure S24a, d and e) was prepared by sequential deposition of a  $\text{SiO}_2$  and a ZnO nanoparticle aerosol. This double layered ZnO- $\text{SiO}_2$  FNN structure was converted into a MOF/ $\text{SiO}_2$ -FNN bilayer via the introduced approach at 150  $^\circ\text{C}$  resulting in a ZIF-8 monolith with thickness of *ca* 12  $\mu\text{m}$  (Figure S24f-i), while the  $\text{SiO}_2$  FNN remained almost unaffected (Figure S24e-f). A polymer blade thinner ( $< 20 \mu\text{m}$ ) than the  $\text{SiO}_2$  layer was adopted to suspend the ZIF-8 monoliths, resulting in their physically peel-off from substrate in the air (Figure S24b, c, insets). The detached ZIF-8 monoliths possess some unique properties including a square centimetre scale top surface area, medium-free transport and self-standing features (Figure S24b, c, insets, g-i). SEM images (Figure S24d-f) further confirm the integral MOF peeling off with only tiny amount of  $\text{SiO}_2$  nanoparticles left on the MOF bottom side (Figure S24g-i). This guaranteed the detaching of MOF monoliths.



**Figure S24** Schematic of the approach for fabrication of self-standing MOF monoliths, and SEM images of a representative 12  $\mu\text{m}$  thick self-standing ZIF-8 monolith. **a-c**, Procedure applied to detach thin ZIF-8 monoliths from Si substrate and photos of an exemplary detached thin self-

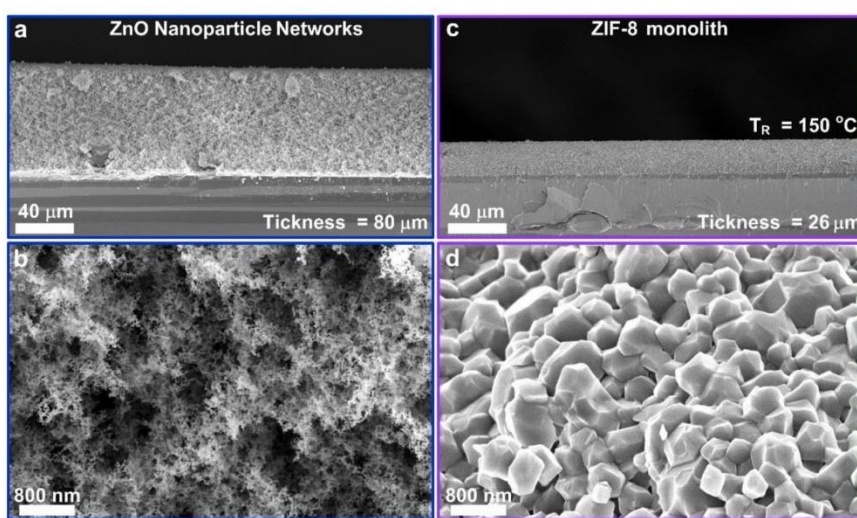
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standing ZIF-8 monoliths. **d-e**, SEM images of the two well-separated ZnO and SiO<sub>2</sub> FNNs. **f**, SEM images of **d** and **e** after conversion resulting in well-separated ZIF-8 and SiO<sub>2</sub> layers. **g-i**, SEM images of an exemplary self-standing thin ZIF-8 monolith of *ca* 12  $\mu\text{m}$ . All samples were coated with a thin layer of Pt (*ca* 2 nm) to avoid charging.



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A ZIF-8 monolith, with an identical thickness to the one employed as separator within the self-standing MOF interlayered Li-S cell (SMILC) batteries, has been prepared on a Si wafer. The as prepared ZnO FNN precursor is *ca* 67  $\mu\text{m}$  in thickness. After conversion in presence of 2-MIM vapours at 150  $^{\circ}\text{C}$  for 18 hours, it resulted in a pure ZIF-8 monolith (*ca* 23  $\mu\text{m}$  thick). The densification factor of *ca* 2.9 was also in line with our previous observations on film densification from a *ca* 7.1  $\mu\text{m}$  thick ZnO FNN to ZIF-8 monolithic films (*ca* 2.8).



**Figure S25** SEM images of the precursor ZnO FNN and the converted ZIF-8 membrane. **a**, SEM images of as prepared ZnO FNN precursor and **(b)** the corresponding higher magnification SEM image of **a**. **c**, SEM images of the converted pure ZIF-8 monolith from **a** and **(d)** the corresponding higher magnification SEM image of **c**. All samples were coated with a thin layer of Pt (*ca* 2 nm) to avoid charging.



**Li-S system**

Relying on its earth abundance and environmental friendliness,<sup>[10, 11]</sup> Sulfur is one of the most promising and visited cathode candidates for high-energy-density rechargeable batteries,<sup>[11-13]</sup> providing, amongst other benefits, a very high theoretical capacity of 1,675 mAhg<sup>-1</sup> and energy density of *ca* 2,500 Whkg<sup>-1</sup>. The latter is about five times higher than that possible with conventional lithium-ion battery technology, based on conventional intercalation reactions.<sup>[11]</sup> As the limited maximal capacity and energy density of conventional lithium-ion battery technology are less able to meet the future user demands such as electrical vehicles and grid storage.<sup>[14, 15]</sup>

**Further characterizations of the batteries**

Given the electrochemical impedance spectra of the SMILC in the frequency range of 1.0 MHz to 0.1 Hz (**Figure 4g**), the high-frequency region is attributed to charge transfer resistance. It is noticeable that a significant semicircle shrinkage of about 94.6% occurred after the first cycle. The large initial impedance is tentatively attributed to the inhomogeneous sulfur/SuperP mixture in the cathode and incomplete wetting of MOF film and commercial separator before electrochemical cycling, while the slow decrease in impedance after the second cycles may result from the migration of active materials to more electrically favourable locations during discharge/charge process.<sup>[16]</sup>

While the poor performance of the bare commercial separators arise from their large pore size,<sup>[17]</sup> the poor cyclability of the cells with a supported MOFs membrane, made by FNN conversion, is tentatively attributed to the trapping of electrolyte and soluble LiPSs in the glass-fiber paper used as support. The overall worse performance and faster capacity decay of the cells with a wet-made MOFs membrane may arise from the lack of a continuous structure. The meso-macropores and cracks of these wet-made MOFs films may not be able to effectively reduce the shuttling of LiPSs, resulting in a similar capacity decay as in the case of the commercial separator. It is also supported by their poor CE (Supplementary Figure S26). In addition, the negligible absorption capability of ZIF-8 to LiPSs<sup>[18]</sup> as well as the structural uniformity of our monoliths ensures the low LiPSs loss and improved cycling stability.

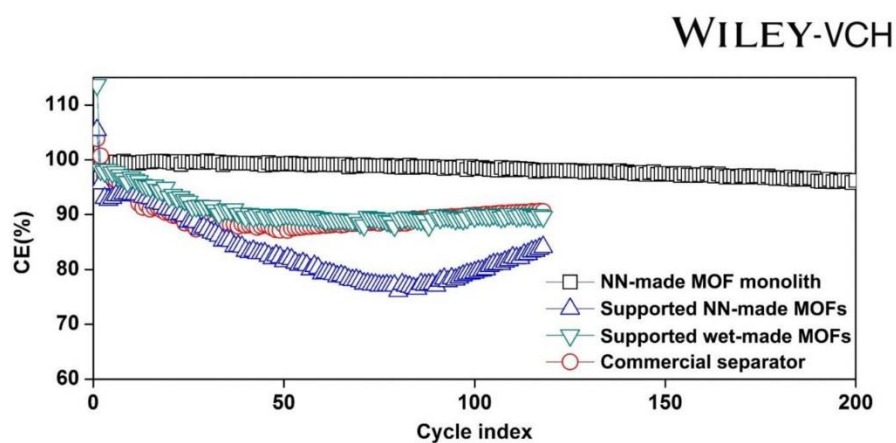


Figure S26 Comparison of Coulombic efficiencies of the batteries with the monolithic MOF membrane and other separators.

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The ZIF-8 monolith alone has no obvious redox reaction with lithium in the voltage range of 1.5 V–2.8 V vs.  $\text{Li/Li}^+$ . This indicates that the majority of the SMILC capacity should be originated from the electrochemical reactions between lithium and sulfur/sulfides and the battery performance will only depends on the suppression of the shuttle effect of soluble  $\text{LiPSs}$ .<sup>[12, 15, 19]</sup>

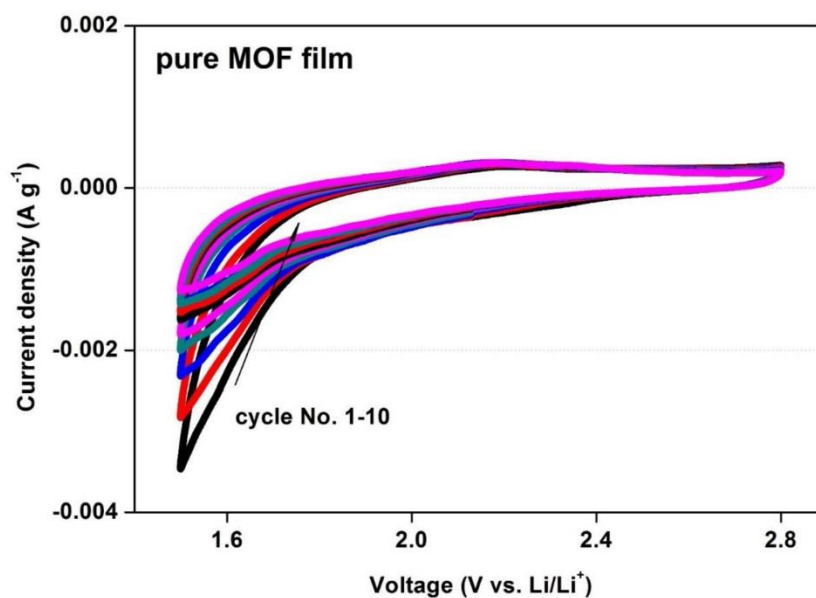
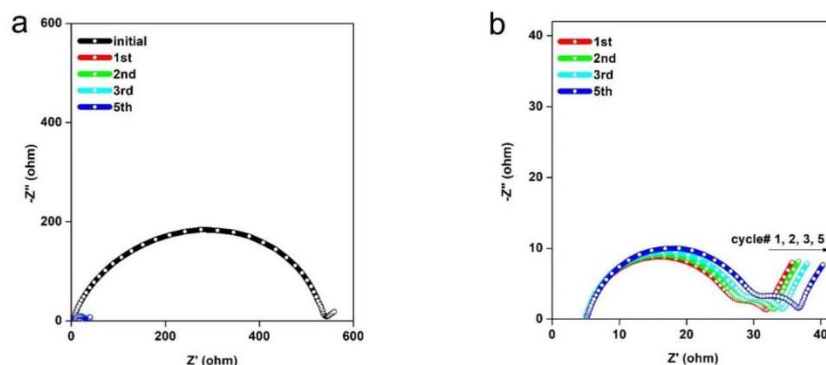


Figure S27 Cyclic voltammogram of a control cell with only ZIF-8 monolith as a cathode and Al foil as the current collector for the first 10 cycles.

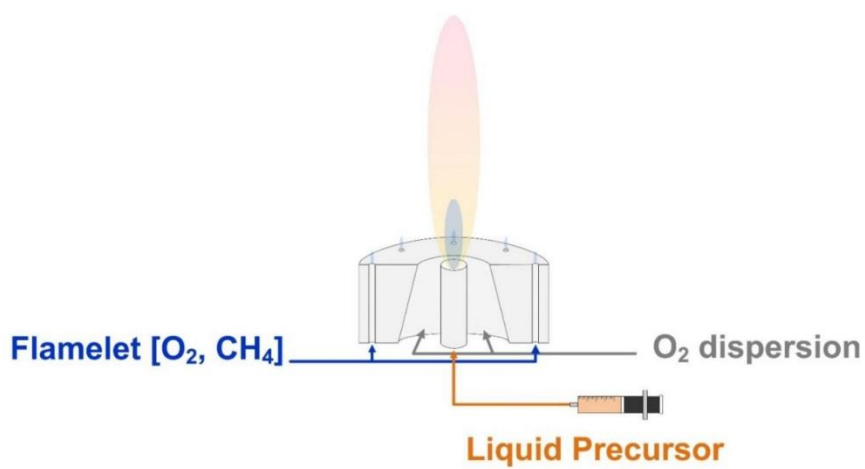
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Similar to the SMILC situation, there is also an obvious impedance drop from the initial state to the one after the 1<sup>st</sup> cycle. This suggests a decreased charge transfer resistance after electrochemical cycling. It is noticeable in Figure S28a that the Li–S battery without MOF interlayer has slightly smaller initial impedance than the SMILC (**Figure 4g**). This might be due to the incomplete wetting of the MOF membrane,<sup>[16, 17, 20]</sup> which resulted in higher charge transfer resistance before electrochemical cycling. Besides, as shown in Figure S28b, there are two semicircles in the high- and medium-frequency regions as well as an obvious increment of both semicircles from the 1<sup>st</sup> to the 5<sup>th</sup> cycle. These two phenomena did not happen for the SMILC. The two semicircles located in the high- and medium-frequency regions in the EIS plots could be attributed to the charge-transfer resistance and surface film impedance, respectively. It has been proposed that the additional surface film impedance could be originated from deposition of  $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$  on Li metal surface due to severe LiPSs shuttle effect in the control battery. The increment of semicircles with cycle number could be due to the gradual growing of additional solid-electrolyte interface (SEI) layer by the deposition of  $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$  on Li anode during cycling.



**Figure S28** EIS plots of the control Li–S battery. **a**, EIS plots of the control Li–S battery at the initial state and cycles 1, 2, 3, and 5. **b**, A zoom-in view of EIS plots of cycles 1, 2, 3, and 5.

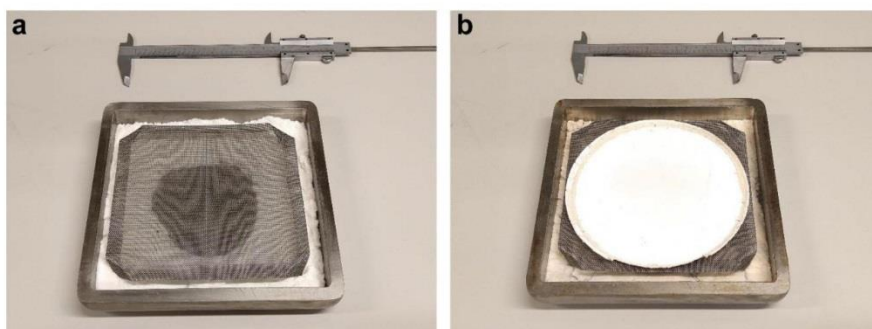
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**Figure S29 Schematic of the flame spray pyrolysis system** used for the synthesis of the precursor ceramic nanoparticles and their self-assembly into a nanoparticle network (FNN).

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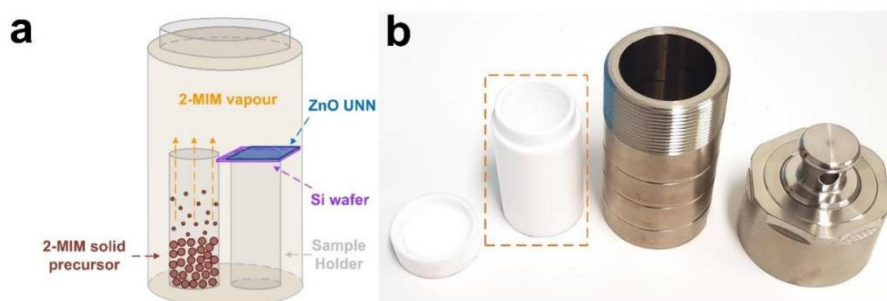
Setup for reaction of the large ZnO FNN: A circular membrane (diameter: 15 cm) with ZnO FNN deposited on one side was placed in a stainless steel reaction chamber ( $16.5 \times 16.5 \times 2$  cm of internal space, wall thickness of 1 cm, with a stainless steel cover lid of  $20 \times 20 \times 1$  cm), with the ZnO layer facing up. The chamber was pre-filled with 15 g of 2-MIM placed at the bottom of the internal space, leaving the middle area empty. The membrane was placed over a wire net ( $15 \times 15$  cm), in order to leave about 1 cm of space between the membrane and the bottom of the chamber, avoiding direct contact with the ligand powder. The chamber was sealed with a little amount of vacuum grease, to avoid leakage of ligand vapours, then placed in an oven at 120 °C for 18 hours. After the reaction time, the chamber was left to cool down to room temperature naturally before opening. The converted ZIF-8 membrane became more rigid after the conversion.



**Figure S30 Optical images of a customized conversion reactor.** **a**, Photograph of the customized conversion reactor filled with 2-MIM solid crystals before reaction. **b**, Photo of the customized conversion reactor opened after reaction with a 15 cm pure ZIF-8 membrane inside.

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A Teflon lined stainless steel autoclave vial as shown in Figure S31 was adopted for our proposed approach.



**Figure S31** Teflon lined stainless steel autoclave vial. **a**, Schematic of the conversion setup. **b**, Photograph of setup accessories.

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**Calculations**

The minimum required extrinsic porosity ( $P_{\min}$ ) for a full conversion from a ZnO FNN precursor to a ZIF-8 monolith is calculated using the following equation:

$$P_{\min} = (1 - 1/R_{\text{Exp}}) \times 100\% \quad (1)$$

where  $R_{\text{Exp}}$  is the 17 folds' volumetric expansion factor from the wurtzite ZnO to ZIF-8 structure. This indicates, to achieve a full conversion, the minimum required extrinsic porosity from a ZnO FNN precursor lies at *ca* 94.12%.

The densification factor ( $C_d$ ) from a ZnO FNN precursor to a ZIF-8 monolithic films at varied temperatures can be obtained via SEM analysis before and after reaction using the following equation:

$$C_d = T_{\text{NN}}/T_{\text{MOF}} \quad (2)$$

where  $T_{\text{MOF}}$  is the thickness of ZIF-8 monolithic films after vapour reaction at varied temperatures (Figure S14b, c, g, h and i, 90 – 150 °C) and  $T_{\text{NN}}$  is the thickness of ZnO FNN precursors before reaction (Figure S14a).

The extrinsic porosities of the converted ZIF-8 monolithic films at varied temperatures (90 – 150 °C) are obtained from calculations via two different approaches: (i) calculations ( $P_C$ ) based on only densification factors of the obtained ZIF-8 monolithic films at different temperatures (90 – 150 °C) derived from SEM thickness analysis, and (ii) calculations ( $P_M$ ) based on SEM and gravimetric analysis of Si wafer sections before and after the ZIF-8 monolithic film growth as reported elsewhere.<sup>[21]</sup>

$P_C$  is determined using the following Equation (3):

$$P_C = [1 - (1 - P_{\text{NN}}) \times R_{\text{Exp}} \times C_d / 100] \times 100\% \quad (3)$$

where  $P_{\text{NN}}$  is the extrinsic porosity of ZnO FNN precursors,  $R_{\text{Exp}}$  is the volumetric expansion factor from wurtzite ZnO to ZIF-8, and  $C_d$  is the densification factor from ZnO FNNs to ZIF-8 monolithic films.

$P_M$  is determined using the following Equation (4):

$$P_M = [1 - (M_{\text{Film\_MOF}}/\rho_{\text{MOF}}/A_{\text{Surface}})/T_{\text{SEM}}] \times 100\% \quad (4)$$



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where  $M_{\text{Film}}$  is the mass of a ZIF-8 monolithic film after conversion at a certain temperature (temperature ranging from 90 to 150 °C),  $\rho_{\text{MOF}}$  is the density of ZIF-8,  $A_{\text{Surface}}$  is the surface area of the measured ZIF-8 monolithic films converted at each temperature, and  $T_{\text{SEM}}$  is the SEM thickness of ZIF-8 monolithic films converted at each temperature. Notably, the extrinsic porosity calculated using both approaches (i and ii) with over 20 batches are in line with each other as shown in Table S1, indicating a very good reproducibility and precisely controlled MOF extrinsic porosity via our proposed ceramic-to-MOF approach.

For instance, given the unvaried film thickness observed after vapour reaction at 90 °C, the extrinsic porosity of the resulting ZIF-8 monolithic film can be simply determined by the volumetric expansion of the primary crystal lattice from the wurtzite ZnO to ZIF-8 as followings:

$$P_C = [1 - (1 - P_{\text{NN}}/100) \times R_{\text{Exp}}] \times 100\% \quad (5)$$

where  $R_{\text{Exp}}$  is the 17 folds' volumetric expansion factor from the wurtzite ZnO to ZIF-8.  $P_{\text{NN}}$  is the porosity of the ZnO FNN precursor.

According to the applied optimal ZnO FNN extrinsic porosity of 98% and the above Equation (5), it would result in a ZIF-8 monolithic film with an extrinsic porosity of 66% which is in line with the obtained extrinsic porosities of  $68 \pm 2\%$  from our ZIF-8 monolithic film (at 90 °C) via calculation approach ii (Equation 4). In fact, Equation (5) is a simplification of Equation (3) where  $C_d = 1$ .

The effect of the reaction temperature on the resulting morphology and ZIF-8 extrinsic porosity can be attributed to the competition between Zn ion diffusion and reaction rate with 2-MIM. At low reaction temperatures the diffusivity of the Zn ions is limited resulting in a localized conversion. Increasing the temperature increases the Zn ion mobility and extent of reaction diffusion (RD),<sup>[22]</sup> as a result, the original network collapses into a more dense ZIF-8 monolith. The measured lower limit of the extrinsic porosity of *ca* 4% (at 150 °C) can be attributed to the closing of the meso and macro-pores, which slow the diffusion of the ligands into the inner part of the MOF monoliths, and may also result in trapping of some air pockets.

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Further characterizations of the porous structure of these ZIF-8 monoliths were pursued by Brunauer-Emmett-Teller (BET) (Supplementary Table S1). These were carried out on both the ZIF-8 monoliths (*ca* 230  $\mu\text{m}$  thick) made by the proposed ceramic-to-MOF approach, and on ZIF-8 particles of *ca* 250 nm in diameter synthesized using an aqueous synthesis. The BET SSA ( $S_{\text{F,BET}}$ ) of the ZIF-8 monoliths (*ca* 230  $\mu\text{m}$  thick) made by the ceramic-to-MOF conversion process was  $1688 \text{ m}^2\text{g}^{-1}$ , which is in agreement with the previous reports as well as the values obtained for control samples ( $S_{\text{P,BET}}$ ) consisting of ZIF-8 particles of *ca* 250 nm in diameter, synthesized using an aqueous synthesis method (Supplementary Table S1).

All the values mentioned above and in **Calculations** section are shown in Table S1.

**Table S1 Table of extrinsic porosity calculations and  $\text{N}_2$  adsorption analysis.**

ZIF-8 monolithic films' extrinsic porosities at varied temperatures ( $T_{\text{R}}$ ) obtained from approach i ( $P_{\text{C}}$ ) and approach ii ( $P_{\text{M}}$ ), BET surface areas ( $S_{\text{P,BET}}$ ) of ZIF-8 particles synthesized using an aqueous synthesis method and self-standing ZIF-8 monoliths of *ca* 230  $\mu\text{m}$  ( $S_{\text{F,BET}}$ ) converted at 150  $^{\circ}\text{C}$ .

| $T_{\text{R}}$         | $P_{\text{C}}$ | $P_{\text{M}}$ | BET                             |                                 |
|------------------------|----------------|----------------|---------------------------------|---------------------------------|
| 90 $^{\circ}\text{C}$  | $66 \pm 2\%$   | $68 \pm 2\%$   | $S_{\text{P,BET}}$              | $S_{\text{F,BET}}$              |
| 100 $^{\circ}\text{C}$ | $43 \pm 2\%$   | $46 \pm 2\%$   |                                 |                                 |
| 110 $^{\circ}\text{C}$ | $27 \pm 2\%$   | $26 \pm 2\%$   |                                 |                                 |
| 120 $^{\circ}\text{C}$ | $11 \pm 2\%$   | $11 \pm 2\%$   | $1555 \text{ m}^2\text{g}^{-1}$ | $1688 \text{ m}^2\text{g}^{-1}$ |
| 150 $^{\circ}\text{C}$ | $4 \pm 2\%$    | $4 \pm 2\%$    |                                 |                                 |

Table S2 Performance comparison of Li-S batteries with MOF-based separators.

| Separator                                                           | Morphology              | S loading<br>[mg cm <sup>-2</sup> ] | Initial<br>capacity<br>[mAh g <sup>-1</sup> ] | Cycle number<br>(retention) | C-rate | Ref.             |
|---------------------------------------------------------------------|-------------------------|-------------------------------------|-----------------------------------------------|-----------------------------|--------|------------------|
| <b>Self-standing ZIF-8 film</b>                                     | Free-standing monoliths | 2.0 – 2.5                           | 1276                                          | 200 (76%)                   | 0.4C   | <b>This work</b> |
| <b>Filtration-growth Ni<sub>3</sub>(HITP)<sub>2</sub>/PP</b>        | sheets                  | -                                   | ~ 900                                         | 300 (65%)                   | 0.5C   | [23]             |
| <b>Ce-UiO-66-BPDC/CNTs/PP</b>                                       | powdery form            | 2.5                                 | 701.8                                         | 800 (49.8%)                 | 1C     | [24]             |
| <b>Ce-MOF-808/CNTs/PP</b>                                           |                         |                                     | 1021.8                                        | 800 (82.1%)                 |        |                  |
| <b>UiO-66-NH<sub>2</sub>@SiO<sub>2</sub></b>                        | powdery form            | 0.5                                 | 1400                                          | 100 (42.9%)                 | 0.1C   | [25]             |
| <b>Mn-BTC/PP</b>                                                    | powdery form            | -                                   | 1430                                          | 80 (76.9%)                  | 0.1C   | [26]             |
| <b>UiO-66/Nafion hybrid-coated</b>                                  | powdery form            | 1.7                                 | 1127.4                                        | 200 (75.5%)                 | 0.1C   | [27]             |
| <b>CNT@ZIF-30/PP</b>                                                | carbon nanotubes        | ca 1.2                              | 1588.4                                        | 100 (54.8%)                 | 0.2C   | [28]             |
| <b>CNT@ZIF-45/PP</b>                                                |                         |                                     | 1374.2                                        | 100 (51.7%)                 |        |                  |
| <b>Interface-induced-growth Ni<sub>3</sub>(HITP)<sub>2</sub>/PP</b> | sheets                  | 3.5                                 | 1224                                          | 100 (92%)                   | 0.2C   | [29]             |
|                                                                     |                         |                                     | 851                                           | 500 (84%)                   | 1C     |                  |
| <b>Y-FTZB/PP/CNT</b>                                                | powdery form            | ca 1.0                              | 1101                                          | 300 (50.6%)                 | 0.25C  | [30]             |
| <b>ZIF-7/PP/CNT</b>                                                 | powdery form            | ca 1.0                              | 1032                                          | 300 (43.8%)                 |        |                  |
| <b>ZIF-8/PP/CNT</b>                                                 | powdery form            | ca 1.0                              | 1025                                          | 300 (39.3%)                 |        |                  |
| <b>HKUST-1/PP/CNT</b>                                               | powdery form            | ca 1.0                              | 989                                           | 300 (19.9%)                 |        |                  |
| <b>Micro/nanosized HKUST-1@GO/PP</b>                                | powdery form            | 0.6 - 0.8                           | 1126                                          | 500 (70.9%)                 | 0.5C   | [31]             |

We have included a detailed table (Supplementary Table S2) comparing the performance of our as-obtained self-standing ZIF-8 separator with other MOF-based separators recently reported. When comparing with other MOF-based separators (Supplementary Table S2), our self-standing ZIF-8 separator shows a superior cycling performance (76% retention after 200 cycles) with a relatively high S loading of 2.0 – 2.5 mg cm<sup>-2</sup> and an initial capacity of 1276 mAh g<sup>-1</sup> under a comparatively high charging-discharging rate (0.4 C), see Supplementary Table S2. For

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example, the interface-induced-grown  $\text{Ni}_3(\text{HITP})_2/\text{PP}$  separators,<sup>[29]</sup> which could afford the highest S loading of  $3.5 \text{ mg cm}^{-2}$ , achieved lower initial capacities of 1224 and  $851 \text{ mAh g}^{-1}$  respectively. The  $\text{CNT@ZIF-30}/\text{PP}$  separators,<sup>[28]</sup> which afforded a higher initial capacity of  $1588.4 \text{ mAh g}^{-1}$ , had relatively low retention of 54.8% after only 100 cycles at a lower charging-discharging rate of 0.2 C. The  $\text{Ce-MOF-808}/\text{CNTs}/\text{PP}$  separators,<sup>[24]</sup> which presented a good cycling performance with a retention of 82.1%, however, experienced a *ca* 20% drop of initial capacity ( $1021.8 \text{ mAh g}^{-1}$ ). Therefore, taking all the different parameters into consideration (i.e. S loading, initial capacity, retention and charging-discharging rate), our self-standing ZIF-8 separators show among the best sets of properties (Supplementary Table S2). In addition, when comparing with other separators (e.g. powdery formed films or filtration-grown sheets), our self-standing ZIF-8 separators could prevent the leaking of LiPSs and enhance the battery performance. A disadvantage of thin ZIF-8 monolithic membranes is the typical brittleness of MOF materials, which results in a reduced mechanical robustness than other membranes made of more robust materials (e.g. CNT or GO). However, the optimization of the ZIF-8 membrane thickness to  $23 \text{ }\mu\text{m}$  resulted in sufficient mechanical properties for both the assembly of the battery and the long-term cycling test.

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**The effect of pressure on the ZIF-8 film**

With respect to the effect of pressure in the ZnO to ZIF-8 (Zn(2-MIM) with sod topology) conversion, we have now calculated the saturation pressure of 2-MIM at all tested temperatures including 90, 100, 110, 120 and 150 °C using Antoine's Equation firstly, in line with previous reports.<sup>[2,32]</sup>

$$\log p = A - \frac{B}{T}$$

Where  $p$  is the saturation pressure (here  $P_{\text{sat}}$ ) in Pa,  $T$  is the temperature in Kelvin (K),  $A$  and  $B$  are Antoine's constants of 2-MIM ( $A = 14.30$  and  $B = 4608.90^{[32]}$ ), respectively. After calculating the saturation pressure of 2-MIM at different temperatures, the amount of solid MOF ligand required to create a vapour of saturation pressure has been estimated using ideal gas equation:

$$PV = nRT$$

where  $P$  used in the equation can be expressed as saturation pressure ( $P_{\text{sat}}$ ),  $V$  is the volume of our reaction chamber (i.e. 80 ml),  $R$  is the ideal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the temperature in Kelvin (K) and  $n$  is the amount of 2-MIM in moles, respectively. The calculated results are shown in the following table:

**Table S3.** Saturation vapour pressure ( $P_{\text{sat}}$ ) and required mass of 2-MIM ligand at different temperatures.

| <b>T (temperature)/°C</b> | <b><math>P_{\text{sat}}</math> (saturation pressure)/Pa</b> | <b>m (mass required)/mg</b> |
|---------------------------|-------------------------------------------------------------|-----------------------------|
| 90                        | 40.11                                                       | 0.09                        |
| 100                       | 87.84                                                       | 0.19                        |
| 110                       | 184.64                                                      | 0.38                        |
| 120                       | 373.70                                                      | 0.75                        |
| 150                       | 2536.62                                                     | 4.74                        |

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As shown above, a tiny amount of 2-MIM is enough to reach the vapour saturation pressure at all listed temperatures. In our experiments, the typical ZnO mass is around 0.6 to 0.8 mg, thus the theoretical stoichiometric amount of 2-MIM needed is in the 1.2-1.6 mg range for the full conversion to ZIF-8. However, in our experiments, we used an amount of 2-MIM in the range of several hundred milligrams to reach and maintain  $P > P_{\text{sat}}$  throughout all the gas phase conversions.

According to the accuracy related to the amount of 2-MIM needed to reach  $P_{\text{sat}}$  at different temperatures, we selected 150 °C as a conversion temperature to examine the effect of the ligand vapour pressure. At 150 °C, by decreasing the amount of 2-MIM from 100 mg to 2 mg a ligand vapour pressure of  $P_{2\text{mg}@150} = 1070.90$  Pa was obtained; this pressure is less than half that of the saturation pressure ( $P_{2\text{mg}@150} = 0.42 P_{\text{sat}@150}$ ). Notably, upon the standard 18 h reaction time at 150 °C at this lower ligand pressure ( $P_{2\text{mg}@150} = 1070.90$  Pa), the ZnO was not fully converted to ZIF-8 (Figure S32, below). As such, our data show that for  $P \geq P_{\text{sat}}$ , an excess of 2-MIM does not influence the ZnO to ZIF-8 conversion. Instead, for  $P < P_{\text{sat}}$  only a partial conversion from ZnO to ZIF-8 is observed.

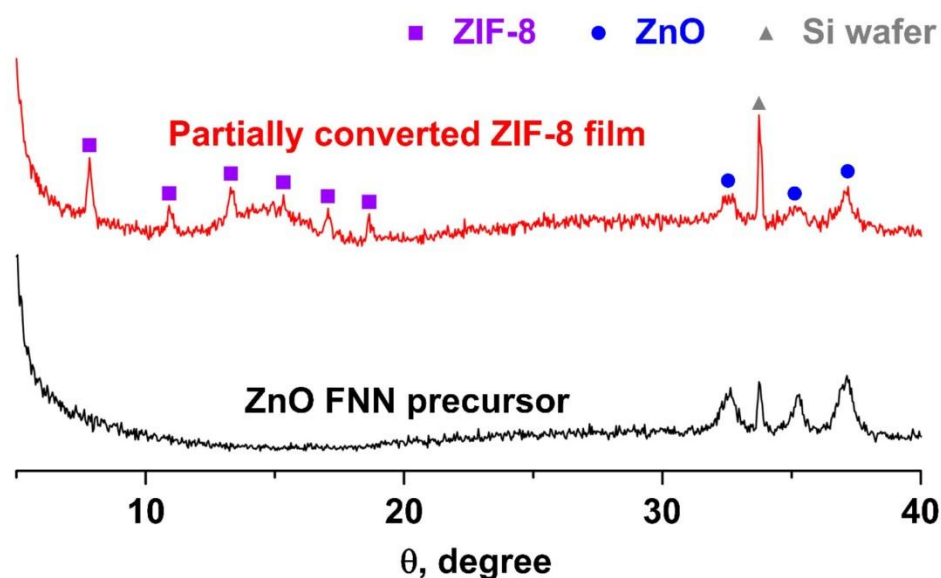


Figure S32 XRD of partially converted FNN precursor at 150 °C under an unsaturated pressure of 1070.90 Pa.

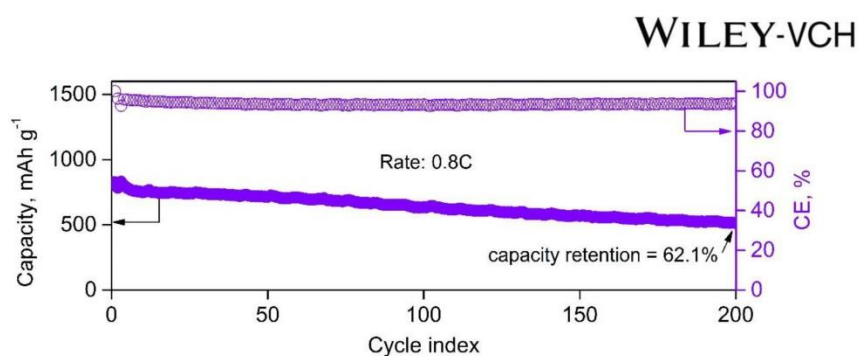
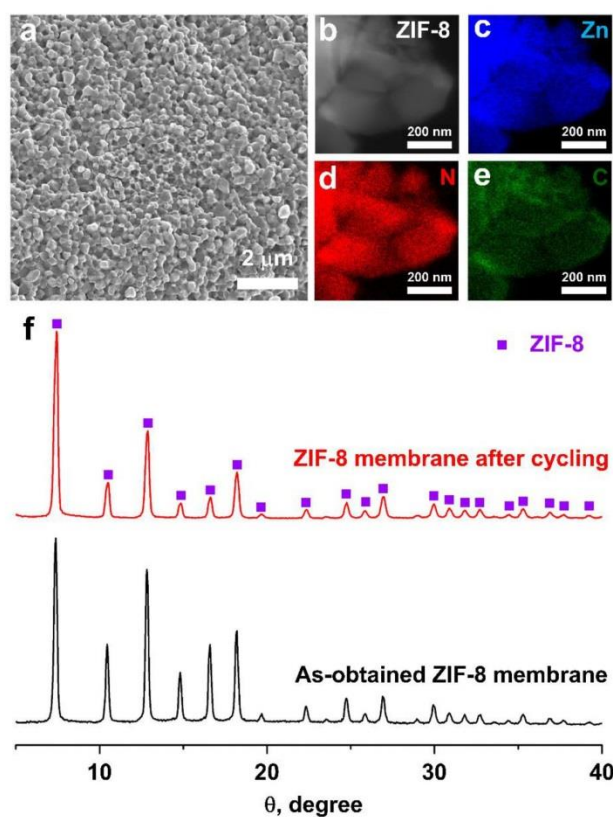


Figure S33 Cycling performance of self-standing ZIF-8 separator at a discharge rate of 0.8 C.



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**Figure S34 Post battery characterizations.** **a**, Cross-sectional SEM images of self-standing ZIF-8 membrane after 200 cycles. **b-e**, HRTEM images of ZIF-8 particles detached from self-standing ZIF-8 membrane after 200 cycles (**b**) and elemental mapping (**c-e**). Zn, N and C are presented in blue, red and green, respectively. **f**, X-Ray diffraction pattern of ZIF-8 membrane before (black line) and after 200 cycles (red line).



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