Development of Nanocomposites Based on Metal–Organic Frameworks and Three-Dimensionally Ordered Macroporous Materials as Potential Catalysts and Structural Materials

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Dedication

To my dearest parents
Abstract

Due to the presence of nanosized features, some properties of nanocomposites can be drastically improved compared to the individual components. As a result, nanocomposites are attractive in many fields, including energy storage, energy conversion, and catalysis. This dissertation focuses on the development of functional nanocomposites using metal–organic frameworks (MOFs) and three-dimensionally ordered macroporous (3DOM) materials. Three major topics are covered in this thesis research.

This dissertation begins with an investigation of the influence of phase purity and pore reinforcement on the mechanical properties of NU-1000 MOF particles. The overall goal of this work is to develop methods of enhancing the mechanical strength of MOFs for practical applications, where densification is likely needed. By flat punch nanoindentation and finite element simulation, the elastic modulus of NU-1000 was found to increase by nearly an order of magnitude through maintaining phase purity and minimizing structural defects. Additionally, introduction of silica into the mesopores of NU-1000 significantly increased the load at failure of NU-1000 particles from 2000 μN to 3000–4000 μN. The results of this work suggest two potential MOF engineering pathways, namely, increasing the phase purity and introducing pore reinforcement to generate more robust MOFs.

The second part of this dissertation describes new approaches of fabricating nanohybrids containing sub-nanosized clusters through nanocasting MOFs as potential catalysts. The purpose of this work is to preserve the catalytically active clusters in MOF materials at high temperatures by replacing the original organic framework with a more robust support, while the ordered and porous structures are maintained. In this context, two
types of nanocomposites (a silica–oxocerium cluster nanohybrid and a carbon–oxozirconium cluster nanohybrid) were synthesized. Preservation of the clusters in both systems was proved by multiple characterization techniques, including XRD, TEM, Raman spectroscopy, and pair distribution function (PDF) analysis. In terms of the potential catalytic abilities, the silica–oxocerium cluster nanohybrid material has a remarkably high loading of cerium (51 wt%) and exhibits redox activity at 750 °C without aggregation, which are properties of interest for high-temperature redox catalysis. The carbon–oxozirconium cluster nanohybrid exhibits a relatively high surface area (266 m²/g), and moderate electrical conductivity (0.41 S/m), which are properties of interest for electrochemical catalysis.

The last part of this dissertation focuses on the synthesis and mechanical properties of 3DOM tungsten (W) and a 3DOM tungsten–silicon oxycarbide (W–SiOC) nanocomposite. The purpose of this work is to investigate the possibility of applying architected materials as strong and low-density structural nanomaterials. Another goal is to fabricate a well-designed microstructure based on the 3DOM matrix. By micropillar compression, the yield strength of ligaments in 3DOM W was measured to be 6.1 GPa, ~6× yield strength of coarse-grained W. The 3DOM W was then used to prepare 3DOM W–SiOC, which exhibited an ordered, interpenetrating, and periodic 3D structure. The maximum stress that the 3DOM W–SiOC material could endure was 1.1 GPa at 30 °C, a 20-fold increase compared to the 3DOM W matrix. The results of this work demonstrate that metallic 3DOM structures could exhibit good strength and be used to fabricate other robust interpenetrating nanocomposites.
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matrix) = \text{Vol(W ligaments)} + \text{Vol(silicon oxycarbide)} + \text{Vol(free carbon)} + \text{Vol(micro and meso pores)} + \text{Vol(large voids)}. The volumes of different components in 3DOM W–SiOC were calculated on the basis of their relative mass percentages and bulk density values. The volume of 3DOM W matrix was calculated using a 5% relative density of tungsten determined in our previous study. As a result, the overall porosity and density of 3DOM W–SiOC were calculated to be 58% and 1.73 g/cm$^3$.

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Abbreviations and Symbols

3D three dimensions, three-dimensional, or three-dimensionally
3DOM three-dimensionally ordered macroporous
A ampere
Å angstrom
ALD atomic layer deposition
APTA acetylated peroxtungstic acid
at% atomic percent
ATR attenuated total reflectance
BCC body-centered cubic
BDT brittle–ductile transition
BDTT brittle–ductile transition temperature
BET Brunauer–Emmett–Teller
c (prefix) centi (×10⁻²)
°C degree Celsius
DED difference electron density
DFT density function theory
DEF N,N-diethylformamide
DIC digital image correlation
DMF N,N-dimethylformamide
DMSO dimethylsulfoxide

xxx
EDS  energy-dispersive X-ray spectroscopy
EIS  electrochemical impedance spectroscopy
eV   electronvolt
FA   furfuryl alcohol
FEM  finite element modeling
FFT  fast-Fourier-transform
FIB  focused ion beam
FT-IR Fourier-transform infrared spectroscopy
FWHM full-width at half-maximum
g    gram
G (prefix) giga ($\times 10^9$)
h    hour
HAADF high-angle annular dark field
HER  hydrogen evolution reaction
HOMO highest occupied molecular orbital
H$_4$TBAPy 1,3,6,8-tetrakis($p$-benzoic acid)pyrene
IPC  interpenetrating composite
k (prefix) kilo ($\times 10^3$)
K    kelvin
L    liter
LUMO lowest unoccupied molecular orbital
m    meter
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>m (prefix)</td>
<td>milli ($10^{-3}$)</td>
</tr>
<tr>
<td>M (prefix)</td>
<td>mega ($10^6$)</td>
</tr>
<tr>
<td>min</td>
<td>minute</td>
</tr>
<tr>
<td>MMC</td>
<td>metal–matrix composite</td>
</tr>
<tr>
<td>MO</td>
<td>metal oxide</td>
</tr>
<tr>
<td>mol</td>
<td>mole</td>
</tr>
<tr>
<td>MOF</td>
<td>metal–organic framework</td>
</tr>
<tr>
<td>n</td>
<td>nano ($10^{-9}$)</td>
</tr>
<tr>
<td>N</td>
<td>newton</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NLDFT</td>
<td>non-local density function theory</td>
</tr>
<tr>
<td>NP</td>
<td>nanoparticle</td>
</tr>
<tr>
<td>OER</td>
<td>oxygen evolution reaction</td>
</tr>
<tr>
<td>ORR</td>
<td>oxygen reduction reaction</td>
</tr>
<tr>
<td>Pa</td>
<td>pascal</td>
</tr>
<tr>
<td>PDC</td>
<td>polymer-derived ceramic</td>
</tr>
<tr>
<td>PDF</td>
<td>pair distribution function</td>
</tr>
<tr>
<td>PFA</td>
<td>poly(furfuryl alcohol)</td>
</tr>
<tr>
<td>PMMA</td>
<td>polymethyl methacrylate</td>
</tr>
<tr>
<td>QSDFT</td>
<td>quenched solid density function theory</td>
</tr>
<tr>
<td>rad</td>
<td>radian</td>
</tr>
<tr>
<td>RPM</td>
<td>robust porphyrinic metal–organic framework</td>
</tr>
</tbody>
</table>
r-WGS   reverse water-gas shift
s        second
S        siemens
SAED     selected area electron diffraction
SALE     solvent-assisted linker exchange
SEM      scanning electron microscopy
sqrt     square root
STEM     scanning transmission electron microscopy
TEM      transmission electron microscopy
TGA      thermogravimetric analysis
THF      tetrahydrofuran
TMOS     tetramethyl orthosilicate
TOF      turnover frequency
TPD      temperature-programmed desorption
V        voltage
wt%      mass percent
XPS      X-ray photoelectron spectroscopy
XRD      X-ray diffraction
ε        strain
θ        diffraction angle
λ        wavelength
μ (prefix) micro (×10⁻⁶)
\( \rho \)  
 density

\( \Omega \)  
ohm
Chapter 1

Size Effects in Nanomaterials—An Introduction
1.1 Size Effects in Heterogeneous Catalysis

1.1.1 Development of Heterogeneous Catalysts with Small Active Sites

Catalysts are crucial in many chemical processes. They can change the mechanisms of chemical reactions, making them happen at faster rates and under more moderate conditions while not being consumed themselves. It has been reported that catalysts are involved in more than 80% of the industrial processes.¹ Catalysts often have metal centers as the catalytically active components. According to the reacting environment with the reactants, they can be classified into homogeneous catalysts and heterogeneous catalysts.² Homogeneous catalysts are in the same phase as the reactants, and the metal centers are usually combined and supported by organic ligands. In contrast, heterogeneous catalysts are in different phases from the reactants, with the structures of metal centers supported by substrate materials. Compared to homogeneous catalysts, heterogeneous catalysts have lower metal atom utilization rates because the metal species in heterogeneous catalysts are in different environments. Usually only the metal atoms at the surface can act as the catalytic sites. However, heterogeneous catalysts are more easily separated from the products and recycled after the reactions, and they usually are more stable in extreme conditions, such as at high temperatures. Therefore, heterogeneous catalysts are preferred and mainly used in industrial processes.

A focus on the development of heterogeneous catalysts has been to decrease the sizes of their catalytically active components.³⁻⁶ In heterogeneous catalysts, the active metal atoms are the ones at the surface with unsaturated coordination sites, which correspond to fewer than 20% of the total amount of metal atoms.¹⁻⁷⁻⁸ Diminishing the size of the catalytic
component can expose more metal species and increase the atom utilization. In addition, decreasing the size of the catalytically active material can save noble metal resources, such as Pt, Pd, Ru, Rh, and Ir, which are scarce in nature while being under high demand for industrial processes.\textsuperscript{7} In this context, the development of small-sized catalytic sites is imperative for sustainability and cost efficiency.

The development of heterogeneous catalysts experienced a big breakthrough with the blossom of nanoscience and nanotechnology at the early 20\textsuperscript{th} century. Since then, nanomaterials have started to be widely applied in heterogeneous catalysis. To date, most commercial catalysts have nanometer-sized particles (1–20 nm) as the active sites in heterogeneous catalysts.\textsuperscript{3} In addition to nanoparticles, nanoclusters within the size regime of \textasciitilde{}1 nm and single atoms have also been developed as the active site in heterogeneous catalysts.

1.1.2 Single-Atom Heterogeneous Catalysts

In terms of maximizing the atom utilization in heterogeneous catalysts, one can naturally imagine single-atom catalysts as the ultimate form. As their names suggest, single-atom catalysts have catalytically active metal atoms singly dispersed and isolated on substrates. One of the earliest single-atom catalysts was reported in 1999, which had the structure of Pt atoms atomically distributed on a MgO support.\textsuperscript{9} The material exhibited competitive activity against Pt particles towards the propane oxidation reaction. Numerous single-atom heterogeneous catalysts have been developed since then and applied in various practical applications.\textsuperscript{1, 5, 7-8, 10-13} Due to their high atom utilization rate, single-site catalysts
show superior catalytic reactivity towards various important industrial reactions in terms of turnover frequency (TOF, moles of product generated per active site per unit time), such as the water-gas shift reaction,\textsuperscript{14-19} the methanol reforming reaction,\textsuperscript{20-21} oxidation and selective oxidation of alkanes,\textsuperscript{22} and dehydrogenation of propane.\textsuperscript{23}

For the fabrication of single-atom catalysts, the key is to ensure the atomic dispersion of metal species onto the supporting material. The stability of single-atom catalysts depends on the bonding strength between metal atoms and substrate atoms. To date, single-atom catalysts are synthesized mainly through impregnation,\textsuperscript{24-26} co-precipitation,\textsuperscript{6, 14, 27-28} or atomic layer deposition (ALD) method.\textsuperscript{29-33} In an impregnation process, a solution containing the precursor of catalytic metal species is mixed with the supporting material. The metal species are bound to the surface of the supports through ion-exchange or adsorption. Single-atom metal species can be achieved through subsequent heat treatment. For co-precipitation, precursors of the catalysts and the supporting materials are mixed to yield precipitates, which are then heat treated. Single-atom catalytic species are achieved during this process and isolated by the supporting materials.

In the ALD method, a volatile organometallic precursor is usually applied. In a typical ALD cycle, a dose of metal precursor is applied first to react with the anchoring sites on the supporting materials, such as hydroxyl groups and bound to the surface. A dose of H\textsubscript{2} is then applied to reduce the metal complexes into desired atoms.\textsuperscript{34} Modified graphite materials containing nitrogen or oxygen have been demonstrated to be good substrates for ALD processes.\textsuperscript{30-31} The isolated oxygen and nitrogen atoms act as electron donors and the anchoring sites for the metal species. In addition to pre-creating isolated anchor sites,
controlling the cycle number and cycle duration can directly achieve single atoms deposited on non-modified substrates, like SiO$_2$, Al$_2$O$_3$, or TiO$_2$.\textsuperscript{32-33}

A major challenge hindering the development and application of single-site catalysts is the low loadings of active metal atoms on supporting materials. In most reports the loading is less than 0.5 wt\%.\textsuperscript{6, 14, 24-25, 27-28, 30-32} For co-precipitation and ALD on non-modified substrates, the concentration of the metal precursor(s) during the synthesis is usually kept very low in order to guarantee the atomic dispersion of loaded metal species. For impregnation and ALD on modified substrates, only a sparse number of anchoring sites can be achieved on the surface of the supports, resulting in low loadings of metal species. Due to this drawback, the reaction rates per overall mass for single-atom catalysts are often at least one order of magnitude lower than those of their nanoparticle counterparts, although they exhibit very high TOF numbers.\textsuperscript{1}

To address this issue, researchers have tried to modify the surfaces of the supports to generate more open sites for metal atoms to bind to. For example, Choi et al. doped porous carbon with sulfur as the substrate to anchor Pt atoms using an impregnation method.\textsuperscript{26} The resulting single-atom catalyst had a Pt loading of 5 wt\%, compared to less than 1 wt\% commonly achieved with unmodified supports.

\subsection*{1.1.3 Comparison Between Single Atoms, Clusters, and Nanoparticles as Catalysts}

In the early stage of the research on single-atom catalysts, these catalysts were considered superior because they combined the merits of both homogeneous and
heterogeneous catalysts, having a high atom utilization rate and maintaining a different phase from the reactants. However, as more is discovered about single-atom catalysts, people realize that they do not always surpass their nanocluster (less than 20 atoms) or nanoparticle (>1 nm, usually having more than 40 atoms) counterparts in catalytical reactivity, but sometimes perform worse instead, or even remain completely inert towards certain reactions. For example, it was reported that gold atoms exhibited almost two orders of magnitude lower catalytic reactivity towards the reaction of CO oxidation than gold nanoparticles (2–5 nm). Another case was demonstrated by Donoeva et al. for catalyzing cyclohexene oxidation with different gold catalysts. Only gold nanoparticles larger than 2 nm were reactive, whereas smaller gold clusters or atoms showed negligible activity. Several factors have been found to play important roles in determining the reactivity–size relationship of catalysts, including electronic and geometric structures of the catalysts, and catalyst–substrate interactions.

Metals acting as catalysts are usually involved in the reactions via transferring electrons. Therefore, the study of size-dependent electronic structures of nanoclusters or nanoparticles is helpful to understand their size-dependent catalytic reactivities. Boronat et al. investigated how the electronic structures of gold clusters changed with different numbers of atoms inside (Figure 1.1a). They found that Au clusters with atom numbers less than seven have planar structures, in which the frontier orbitals are exposed and fully accessible to incoming reactants. As the atom number increases, the Au clusters become more three-dimensional while more and more Au atoms are buried inside. Those inner Au atoms gradually contribute more to the frontier orbitals, leading to fewer exposed lobes
and weakened reactivity of the clusters. Another difference among the Au clusters is the arrangement of energy levels. With more Au atoms in a cluster, the energy levels transform from discrete to continuous. Additionally, the bandgap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is influenced by the sizes of the clusters. These differences in the electronic structures lead to different catalytic reactivities, especially in photocatalysis.

Taylor et al. demonstrated the relationship between work function and Au cluster size (Figure 1.1b). When the atomicity increases above 70, there is a relatively clear trend indicating that the work function increases with more Au atoms in the clusters. When the atomicity is less than 70, no such correlation is observed. However, with atomicity smaller than 30, the work function of Au clusters is generally smaller than that of clusters with more than 70 atoms. From these observations, it can be concluded that small metal clusters or single atoms often have small work functions and accessible frontier orbitals, so they have high reactivity per atom in catalytic reactions. In contrast, nanoparticles have continuous energy levels and more available electrons to transfer, rendering them widely applicable for a variety of reactions.
Figure 1.1. (a) Optimized structures, calculated frontier orbitals, and energy levels of Au clusters. Obtained at the B3LYP/LANL2DZ level using the Gaussian09 program. Reprinted with permission from ref.43, Copyright (2014), American Chemical Society. (b) Work function-particle size relationship of Au clusters. The work function data was obtained from ultraviolet photoelectron spectroscopy. Reprinted with permission from ref.8, Copyright (2018), American Chemical Society. (c) Relationship between vacancy formation energy and particle size of cerium oxide particles. Reprinted with permission from ref.47, Copyright (2017), American Chemical Society.
When the catalytic species is a metal oxide, the situation is more complex. In addition to transferring electrons during catalysis like metals, metal oxides can also exhibit catalytic reactivity via transferring oxygen ions and forming vacancies.\textsuperscript{48-50} Bruix et al. studied the relationship between vacancy formation energy and the particle size of cerium oxide (Figure 1.1c).\textsuperscript{47,51-53} In their study, Ce\textsubscript{80}O\textsubscript{160} with a particle size around 1.8 nm exhibited the minimum vacancy formation energy.

In terms of geometric structures, the active sites of single-atom catalysts are supported by the substrates, so they usually have a fixed geometry during the reaction. One thing to note is that homogeneous catalysts can show different configurations during the reactions because the bonds between the metal species and the coordinated ligands are more flexible. For metal clusters, a structural transformation during reactions has been suggested from theoretical calculations.\textsuperscript{54-56} Fernández et al. predicted that Au, Ag, and Cu clusters could exhibit different configurations when they have different charges using first-principle calculations.\textsuperscript{54} For example, X\textsubscript{3} (X=Au, Ag, or Cu) exhibits a bent structure, while X\textsuperscript{3−} is linear and X\textsuperscript{3+} is triangular. Additionally, when the number of atoms reaches a certain value, the structure transforms from planar to 3D, which can lead to dramatic changes in the catalytic properties.\textsuperscript{55-56} When the catalytically active parts reach the size of nanoparticles, strains and lattice defects become more dominant factors than geometries on the catalytic reactivities.\textsuperscript{57} Their overall structures are relatively stable during the reactions, while the surface atoms might migrate during the reaction.\textsuperscript{58-59} To date, no conclusion has been reached yet regarding the geometry–reactivity relationship for heterogeneous
catalysts of different sizes. However, the elucidation of the size-dependent geometrical change can provide insights into the studies of specific catalytic reactions.

Catalyst–substrate interactions are a more complex topic compared to the electronic and geometry structure of the catalysts since there are two study subjects. For example, different metal species prefer different locations when they are deposited onto a substrate;\textsuperscript{60} different substrates exhibit different degrees of charge transfer to the supported metals;\textsuperscript{61-62} and different substrates prohibit the sintering of supported metal species to different degrees.\textsuperscript{63-64}

From the discussion above, it can be concluded that single atoms, nanoclusters, and nanoparticles have their unique features in terms of electronic structures, geometric structures, and interactions with the substrates. Generally, one needs to carefully choose the type and size of metal species, and the type of substrate material to achieve the desired reactivity or selectivity towards certain reactions.

1.1.4 Size-dependent Reactivity and Selectivity in Heterogeneous Catalysis

Although much is still unknown about the size-dependent reactivity in heterogeneous catalysis, there has been progress on the study of certain reactions. Two of the most studied cases are the oxygen reduction reaction (ORR) and the reverse water-gas shift (r-WGS) reaction. In those two reactions, one can change the pathway and increase the selectivity towards a preferred product by using either single atoms or nanoparticles as the catalysts.
In ORR, Pt is usually applied as the catalyst. It has been reported that different products form when Pt catalysts of different sizes are used.\textsuperscript{24, 26, 65-66} When Pt nanoparticles are employed, enough electrons can be transferred to the reactant O\textsubscript{2}. Therefore, ORR proceeds in a 4e\textsuperscript{−} pathway, which results in the formation of H\textsubscript{2}O as the main product. When Pt single atoms are used, the dispersed Pt atoms can each transfer only two electrons to the O\textsubscript{2} molecules. Therefore, ORR proceeds in a 2e\textsuperscript{−} pathway and the main product turns to H\textsubscript{2}O\textsubscript{2}.

\[
4H^+ + 4e^- + O_2 \rightarrow 2H_2O
\]

\[
2H^+ + 2e^- + O_2 \rightarrow H_2O_2
\]

The reverse water-gas shift (r-WGS) reaction is another typical case where single atoms and nanoparticles lead to different products. In this process, CO\textsubscript{2} is reduced by H\textsubscript{2} in the presence of Pd, Rh, or Ru as the catalysts. It was observed that Pd and Ru nanoparticles showed high activity towards the formation of CH\textsubscript{4} as the reduction product. However, when Pd and Ru were applied as single atoms, the product changed to CO.\textsuperscript{67-69} This discrepancy resulted from the different interactions between the catalyst and the reactants. In the first step of r-WGS process, CO\textsubscript{2} molecules are reduced to CO in cases of both nanoparticle and single-atom catalysts. The formed CO molecules are inclined to leave the surfaces of single-atom catalysts as the final product. However, they tend to bind onto the surface of nanoparticles because CO can bridge the electron-rich Pd or Ru atoms and create a more stable structure. Therefore, CO was further reduced to CH\textsubscript{4} with nanoparticles as the catalyst.
\[ CO_2 + H_2 \rightarrow CO + H_2O \]

\[ CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \]

1.2 Development of Metal–Organic Frameworks as Heterogeneous Catalysts

1.2.1 Introduction of Metal–Organic Frameworks

Metal–organic framework materials (MOFs), as a relatively new type of solid porous materials, are constructed of nanosized metal (or oxo-metal) nodes or clusters supported and separated by organic linkers. In MOFs, the organic linkers act as the bridging ligands that connect numerous metal ion/oxo-metal cluster nodes, forming a periodic, porous structure. These crystalline materials feature a large number of evenly distributed nanosized clusters, high surface areas, and tunable pores and channels. Additionally, due to the extraordinary flexibility in the choice of building blocks, the number of possible MOF materials with different topologies and pore dimensions is very large. Over 88,000 different structures have been reported in the MOF-subset of the Cambridge Structural Database, among which more than 8,000 are porous, with pore diameters up to 9.8 nm, pore volumes reaching 5.0 cm\(^3\)/g, and BET surface areas as high as 7839 m\(^2\)/g. Because of their structural and compositional diversity, MOFs have shown promise in many applications, including gas storage, chemical separation, catalysis, and sensors.
1.2.2 MOFs and Modified MOFs as Heterogeneous Catalysts

Among different applications of MOFs, catalysis has been extensively studied.\textsuperscript{89-93} Due to their naturally solid phase, MOFs can be separated and recovered after reactions. Therefore, MOFs are classified as heterogeneous catalysts. However, MOFs do not suffer from some of the common drawbacks of traditional heterogeneous catalysts. The catalytically active clusters in MOFs are evenly distributed throughout the structure and accessible to reactants that can diffuse through the pores. In this context, MOFs have the merits of homogeneous catalysts, high utilization rate of the catalytic species, and high reactivity per site.

Compared to single-atom catalysts, the catalytically active sites in MOF materials are often larger clusters composed of several metal atoms or metal and oxygen atoms (usually within 1 nanometer). They are present as the nodes that are connected by organic linkers. The cluster structure can be different depending on the type of metal species and MOF architecture. For example, Zr (IV) or Ce (IV) often form clusters of the type $\text{M}_6\text{O}_8$ ($\text{M} = \text{Zr}$ or Ce) octahedron (NU-1000, UiO-66, MOF-808),\textsuperscript{94-95} while Zn can form Zn$_4$O tetrahedra (MOF-5) or remain a single ion (ZIF),\textsuperscript{96-97} and Cr can form Cr$_3$O (MIL-101) or CrO$_6$ (MIL-53) arrangements.\textsuperscript{98-100} Due to the large variety of clusters that can be accommodated, MOFs are potential candidates for a wide range of catalytic processes. To date, a lot of effort has been committed to testing MOFs as catalysts for different reactions.\textsuperscript{101} Some reported MOFs applied as heterogeneous catalysts are summarized in Table 1.1.
### Table 1.1. Applications of selected MOFs and modified MOFs reported as heterogeneous catalysts for different types of reactions.

<table>
<thead>
<tr>
<th>MOF</th>
<th>reaction</th>
<th>temperature</th>
<th>metal species</th>
</tr>
</thead>
<tbody>
<tr>
<td>UiO-66, UiO-67, MOF-808, NU-1000</td>
<td>hydrolysis of phosphoester-containing compound$^{87,102}$</td>
<td>25°C</td>
<td>Zr</td>
</tr>
<tr>
<td>MIL-101</td>
<td>cyanosilylation reaction$^{99}$</td>
<td>40°C</td>
<td>Cr</td>
</tr>
<tr>
<td></td>
<td>oxidation of tetralin$^{103}$</td>
<td>80°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>oxidative cleavage of alkenes with H$_2$O$_2$$^{104}$</td>
<td>70°C</td>
<td></td>
</tr>
<tr>
<td>Cu-MOF-74</td>
<td>acylation of anisole$^{105}$</td>
<td>120°C</td>
<td>Cu</td>
</tr>
<tr>
<td>Co-ZIF-9</td>
<td>photocatalytic splitting of CO$_2$$^{106}$</td>
<td>110°C</td>
<td>Co</td>
</tr>
<tr>
<td>MIL-100</td>
<td>oxidation of thiophenol$^{107}$</td>
<td>70°C</td>
<td>Fe</td>
</tr>
<tr>
<td>IRMOF-74</td>
<td>hydrogenolysis of aryl-ether compounds$^{108}$</td>
<td>120°C</td>
<td>Mg</td>
</tr>
<tr>
<td>Ni-NU-1000 (ALD)</td>
<td>ethylene hydrogenation$^{109}$</td>
<td>100°C</td>
<td>Ni</td>
</tr>
<tr>
<td>Ni-UiO-66 (ALD)</td>
<td>ethylene hydrogenation$^{110}$</td>
<td>100°C</td>
<td>Ni</td>
</tr>
<tr>
<td>Re-Nu-1000 (ALD)</td>
<td>ethylene hydrogenation$^{111}$</td>
<td>190°C</td>
<td>Re</td>
</tr>
<tr>
<td>Zr-MTBC-CoH</td>
<td>alkene hydrogenation$^{112}$</td>
<td>23–80°C</td>
<td>Co</td>
</tr>
<tr>
<td>Ni-(Fe)MIL-101</td>
<td>selective ethylene dimerization$^{113}$</td>
<td>10°C</td>
<td>Ni</td>
</tr>
<tr>
<td>AuPd-MIL-101</td>
<td>dehydrogenation of formic acid$^{114}$</td>
<td>90°C</td>
<td>Au, Pd</td>
</tr>
<tr>
<td>AuAg-ZIF-8</td>
<td>reduction of 4-nitrophenol$^{115}$</td>
<td>-</td>
<td>Au, Ag</td>
</tr>
</tbody>
</table>

In addition to the intrinsic catalytic properties of their clusters, MOF materials can be used as catalysts in more reactions through further structural modification. The general strategies of MOF engineering include cluster modification, organic linker modification,
and nanoparticle introduction.\textsuperscript{93} For cluster modification, ALD has been proved as a powerful tool. As mentioned in the earlier section, ALD can be used to deposit extra metal species onto supporting materials. MOFs containing Zr\textsubscript{6}O\textsubscript{8} clusters, such as NU-1000 and UIO-66 MOFs, have been reported as good substrates for anchoring other metals.\textsuperscript{109-111, 116-119} With the help of ALD, the target metal atoms, such as Ni, Zn, Al, In, and Re, can be deposited onto the Zr\textsubscript{6}O\textsubscript{8} clusters, and the developed materials exhibit catalytic properties derived from the newly introduced metals. Notably, the number of metal atoms loaded onto the clusters depends greatly on the precursor species and reaction conditions. For example, bis(N,N'-di-tert-butyl-acetamidinato)nickel(II) (Ni(MeC(Nt-Bu)\textsubscript{2})\textsubscript{2}) as the ALD precursor could load single Ni atom on Zr\textsubscript{6}O\textsubscript{8} cluster while trimethylaluminum (AlMe\textsubscript{3}) as the precursor resulted in high loadings of aluminum on each cluster and even caused degradation of the MOF structure; trimethylindium (InMe\textsubscript{3}) as the ALD precursor could load 2 to 6 In atoms on each cluster depending on the reaction temperature.\textsuperscript{117}

In addition to the ALD technique, there are other methods developed to modify Zr(IV) clusters in MOFs, in which the strategies are also using hydroxyl groups on the Zr(IV) clusters as the anchoring sites to introduce metal species.\textsuperscript{112, 120} For example, Ji et al. applied nBuLi to deprotonate the -OH groups on Zr(IV) clusters in UiO-68, then introduced CoCl\textsubscript{2} or FeBr\textsubscript{2} to create Co- or Fe-sites. The product was active towards the reactions of benzylic C-H silylation and borylation.

For modification of organic linkers in MOFs, a well-developed strategy is to create chelating ligands to support and stabilize the introduced metal species through certain chemical processes.\textsuperscript{113, 121-123} The products derived from organic linker modification have
similar chemical environments for metal species to that of homogeneous catalysts. This method can be used on MOFs with clusters not containing -OH groups or MOFs without stable clusters. For example, Canivet et al. applied 2-pyridine carboxaldehyde and nickel (II) chloride to react with the 2-aminoterephthalate linker in MIL-101 MOF, creating a $N,N'$-chelating centered Ni complex. The product exhibited high reactivity and selectivity towards the reaction of liquid-phase dimerization of ethylene to 1-butene.

Another interesting but relatively new method for the modification of organic linkers in MOFs is solvent-assisted linker exchange (SALE). In a typical SALE process, a MOF material is immersed in a concentrated solution containing another type of organic linker. Linker exchange happens between the MOFs and the linkers in the solution, resulting in the incorporation of new linkers into the MOF crystals. This method can introduce new catalytic properties into the original MOFs when the linker molecules in the solution contain the desired metal species. For example, Takaishi et al. reported the replacement of dipyridyl-porphyrin Zn linkers with dipyridyl-porphyrin Al linkers in a robust porphyrinic MOF (RPM) material. Since the original RPM had Zn clusters, it was denoted as ZnZn-RPM and the product was ZnAl-RPM. The ZnAl-RPM material was found to be a good catalyst in epoxide ring-opening by trimethylsilylazide.

For introducing nanoparticles (NPs) into MOFs, a general strategy is to introduce a precursor into the pores of MOFs first, and then condense the precursor to form the nanoparticles. For this purpose, chemical vapor deposition and liquid-phase impregnation methods have been widely applied. In chemical vapor deposition, a gaseous organometallic precursor is employed to diffuse into the pores of MOFs. The precursor is
then reduced in H\textsubscript{2} to form the desired metal nanoparticles. For example, exposing MOF-5 to ($\eta^5$-C\textsubscript{5}H\textsubscript{5})Cu(PMe\textsubscript{3}) vapor, followed by H\textsubscript{2} reduction at 150 °C led to the formation of Cu NP/MOF-5.\textsuperscript{128} With similar procedures, Pd NP/MOF-5 and Au NP/MOF-5 could also be achieved.\textsuperscript{128} For liquid-phase impregnation, the precursors are solutions, usually containing chloride or nitrate slats of the desired metal species. After infiltration and dry, the precursors are reduced, typically by H\textsubscript{2} or NaBH\textsubscript{4} to form metal NPs. Interestingly, due to its relatively facile approach, liquid-phase impregnation has been used to achieve dual-metal NPs/MOF systems, such as AuAg NPs/ZIF-8 and AuPd/MIL-101.\textsuperscript{114-115}

One drawback of chemical vapor deposition and liquid-phase impregnation is their lack of control over the nanoparticle size or spatial distribution. The grown NPs usually show large size deviation, and in some cases, they aggregate on the external surface or grow unexpectedly large inside the pores and block them.\textsuperscript{93} Considering the need for precise control, ALD is a good option, and it has been studied as an advanced tool to achieve uniformly-sized/distributed nanoparticles in MOFs.\textsuperscript{129, 132-133} As discussed earlier, a coordination complex containing the metal species can react with the substrate material and anchor the metal atoms onto it. One can regard this process as the A cycle in ALD, after which single-atom deposition is fulfilled. Another B cycle can be applied after the A cycle, during which a second vapor phase, such as H\textsubscript{2}O, is introduced to react with the deposited metal complex, creating a new hydroxyl group as the anchor site for the next potential A cycle.\textsuperscript{110, 134} Through multiple AB cycles, nanoparticles with desired sizes can be obtained. Meledina et al. demonstrated the deposition of Pt nanoparticles into the pores of MIL-101 MOF through applying (methylcyclopentadienyl)trimethylplatinum
(MeCpPtMe₃) and O₃ in A and B cycles, respectively.¹³² The Pt nanoparticles were mostly confined in the pores of MIL-101 and exhibited uniform sizes as the pore diameter. From the above discussion, it can be seen that the strategy to apply MOFs or MOF-modified materials as catalysts focuses mainly on engineering the metal species and their chemical environment. With the intrinsic highly porous structures, nano-sized features, and almost infinite compositions, the sky is the limit for MOFs as heterogeneous catalysts.

1.2.3 MOF-Derived Nanocomposites as Heterogeneous Catalysts

Although MOFs have proven to be efficient heterogeneous catalysts for many applications, there are still limitations for this type of materials. One drawback of MOF materials is their relatively poor stability. As can be seen in Table 1.1, the applied temperatures of MOF materials are restricted to a relatively low range. Because MOFs are organic–inorganic hybrid materials, they are only stable at moderate temperatures (< 350 °C).¹³⁵ At elevated temperature, and especially in an oxidizing environment, organic linkers in MOFs decompose and the structures collapse, resulting in the aggregation of the catalytically active metal clusters. However, many industrial processes are endothermic, such as alkane dehydrogenation and steam reforming, which have higher product yields at higher temperature.¹³⁶-¹³⁷ Moreover, chemical reactions proceed faster at higher temperatures with higher conversion rates and shorter reaction time. In addition to thermal stability, many MOFs also suffer from poor stability in ambient conditions or even in water, resulting from the large porosity and weak bonding between the clusters and linkers.¹³⁸-¹⁴⁰
To extend the application of the clusters in MOF materials, one approach is to convert the supporting linkers in MOF structures into more robust structures, while the ordered and porous structures and the isolated catalytic clusters are maintained. In order to accomplish this goal, nanocasting has been demonstrated as an efficient method. As its name suggests, nanocasting is casting at the nanoscale. The nanocasting technique has been widely applied to achieve hierarchical nanostructures. For nanocasting, a porous structure is required as the template. Another material as the target is introduced into the pores of the template. Through specific post-treatment, the target forms a rigid network inside the pores, and the template is removed to achieve the nanocast product (Figure 1.2a).
Figure 1.2. (a) Scheme showing the general procedure of nanocasting in a mesoporous silica material. If the amount of precursor is high enough and pores exist between adjacent channels, linkages can form after template removal (the black sticks in the replica figure). Reprinted with permission from ref.142, Copyright (2006), WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Scheme showing the procedure of nanocasting NU-1000 MOF with silica. Zr₆@SiO₂ indicates the final product having the structure of hexa-zirconium (IV) clusters supported on SiO₂. Reprinted with permission from ref.146, Copyright (2016), American Chemical Society.

Malonzo et al. first demonstrated silica nanocasting in NU-1000 in 2016, from which a structure of hexa-zirconium (IV) clusters supported on silica was achieved (Figure 1.2b).135 In the product, the sub-nanometer-sized Zr clusters remained isolated and supported by the silica. Additionally, the nanocast material maintained a large surface area
and high porosity. Since then, the silica nanocasting method has been applied to various MOF materials. Depending on the different stability degrees of the MOFs, nanoclusters or nanoparticles supported on silica were achieved. For example, cerium oxide particles with different sizes supported on silica were obtained from nanocasting different cerium MOFs.

Another drawback of MOFs is their poor electronic conductivity. This limitation hinders their applications in electrocatalysis, although they intrinsically have many merits to be good electrocatalysts, such as large surface area, tunable compositions and porosity, and evenly distributed catalytically active clusters. One strategy to overcome this drawback is turning MOF materials into carbon-based nanomaterials. Indeed, a lot of effort has been expended on this topic in the scientific community. For this purpose of study, the main technique is pyrolysis, turning the organic linkers into carbon. Depending on the composition and morphology of the final products, different types of carbon-based nanomaterials can be obtained. The developed carbon-based nanomaterials have been extensively studied as electrocatalysts in oxygen reduction reactions and hydrogen evolution reactions. Some of them exhibit competitive performance compared to commercial Pt/C materials. More detailed introduction on MOF-derived carbon nanomaterials can be found in Chapter 4.
1.3 Size Effects in Structural Materials

1.3.1 Size-Dependent Mechanical Properties

The effects of size on the structure–reactivity relationships of heterogeneous catalysts have been discussed in the last sections. Moreover, size effects are also an important topic in the study of mechanical properties of materials.\textsuperscript{158} The well-developed Hall-Petch strengthening theory describes the relationship between yield strength and grain size in polycrystalline metal materials (Figure 1.3a).\textsuperscript{159-162} In a polycrystalline metal or metal alloy, adjacent grains usually have different orientations, and dislocations move across the grain boundaries while the material deforms. According to the Hall-Petch theory, the number of grain boundaries increases with decreasing grain size, which further creates larger energy barriers for dislocations to move among grains. The piling-up of dislocations inside the grains hinders the onset of plasticity of the material, therefore increasing its yield strength. When the grain size keeps decreasing and approaches the size of the dislocation inside, the movement of grain boundaries, including rotation, migration, and sliding, starts to dominate the deformation behaviors. In this situation, the material starts to exhibit smaller yield strength with decreased grain size (inverse Hall-Petch strengthening).\textsuperscript{162} The grain size corresponding to this turning point is defined as the critical grain size.\textsuperscript{163} It varies by metal species, but is roughly between 10 and 30 nm.\textsuperscript{163-167}
Figure 1.3. (a) Diagram indicating the relationship between the strength and grain size of a polycrystalline metal or metal alloy material. The strength reaches the maximum at the critical grain size, \( d_c \). When the grain size is larger than \( d_c \), the material exhibits “smaller is stronger” behavior and deforms in a dislocation-mediated pattern. When the grain size is smaller than \( d_c \), the material exhibits “smaller is weaker” behavior and deforms in a grain boundary-mediated pattern. (b) Compressive stress-strain curves of single crystal Nb nano-pillars with different diameters. The SEM images indicate the morphology of an 800 nm single crystal Nb nano-pillar before and after compression. Adapted with permission from ref.167, Copyright (2011), Elsevier Ltd.
In addition to the size-dependent plasticity in polycrystalline metals, another size effect in single crystals, named external geometric size effect, has been widely studied in the last decade.\textsuperscript{167} It was observed that the strength of a single crystalline material scales inversely with the sample dimensions, such as thin film thickness and nano- or micro-pillar diameters (Figure 1.3b).\textsuperscript{167-172} This type of size effect has been reported for sample dimensions from 100 nm to several microns.\textsuperscript{168, 171} For example, Jennings et al. demonstrated that 300 nm Au nanopillars attained strength around 50 times higher than their corresponding bulk form.\textsuperscript{170}

The reason for the occurrence of this type of size effect has not been fully understood, but one developed theory is the “dislocation starvation” theory.\textsuperscript{170, 173-175} According to the dislocation starvation theory, dislocations in a single crystal can self-multiply under a certain critical stress and then lead to deformation of the material. However, the critical stress value increases as the sample size decreases. When the sample becomes very small, the initial dislocations in the material are annihilated at the surface before they can multiply, leaving the material in a state of dislocation starvation. Therefore, a high-pressure load is required to induce the formation of new dislocation sites for the material to deform.

In addition to crystalline materials, size effects have also been observed in amorphous materials.\textsuperscript{176} In one study, Vashisth et al. reported size effects in an amorphous polymer-derived ceramic material. They demonstrated that the strength of SiOC nanofibers increased from ~1 GPa to ~ 3.3 GPa with size decreasing from 1.1 μm to 630 nm. The reason is still unknown, but it can be postulated that as the structure becomes more
complex, there are more impacting factors that influence the size–strength relationship of a material.

### 1.3.2 Cellular Materials

Cellular materials are an important type of structural material, originally found in nature, such as wood, bones, plant stems, and sea sponges.\textsuperscript{177-180} They feature high porosity, low density, and outstanding strength and stiffness. Inspired by these natural architectures, many types of man-made lightweight cellular materials have been developed and applied in different areas, such as structural component, energy absorption, and biomaterials.\textsuperscript{181-183}

The mechanical properties of cellular materials are determined by several factors, including their solid constituent material, relative density, and cellular architecture.\textsuperscript{184} The elastic modulus and the failure strength of a cellular material can be determined by the Gibson–Ashby equations (1 and 2),\textsuperscript{185} in which $E$, $\sigma$, and $\rho$ refer to elastic modulus, failure strength, and density respectively. The subscript $s$ indicates the corresponding property for the solid constituent materials. $C_1$, $C_2$, $n1$, and $n2$ ($C1 \leq 1$ and $n1, n2 \geq 1$) are constants based on the geometry of the structures in terms of the loading direction.

\begin{align*}
E & \approx C_1 \times E_s \times \left(\frac{\rho}{\rho_s}\right)^{n1} \quad (1) \\
\sigma & \approx C_2 \times \sigma_s \times \left(\frac{\rho}{\rho_s}\right)^{n2} \quad (2)
\end{align*}

The Gibson-Ashby equations indicate that the strength and stiffness of cellular materials are intrinsically lower than the corresponding values for their solid constituent
materials due to the low densities. In this context, cellular materials would appear not to be competitive as strong materials. However, considering the needs for energy efficiency and convenience, the quality of being lightweight is as important and desirable as strength in many practical applications, such as bioengineering, aerospace, and automobile industries. Therefore, designing cellular materials with specific architecture to maximize the $C$ value and minimize the $n$ value is important for the development of lightweight cellular materials. Notably, when the sizes of the ligaments in a cellular material become very small, size-dependent strengthening occurs. In that situation, the $E_s$ and $\sigma_s$ values in the Gibson–Ashby equations will change and may exceed the values for the corresponding bulk materials.  

The strength and stiffness of a cellular material increase with increasing structural order (Figure 1.4). For example, $C_2$ for a brittle foam with random porosity is ~0.2, but it becomes ~0.67 for a microlattice, ~0.87 for a pyramidal truss, and 1 for a honeycomb. Thus, the honeycomb structure is the strongest. Due to its anisotropic architecture, the honeycomb structure is often applied in an environment where the loading or the flow direction is predictable. In contrast, lattice structures are more often seen in real life, such as in bridges and buildings.
The mechanical behavior of lattice structures can be estimated by Maxwell’s stability criterion (equation 3), where $M$ is the Maxwell number, $s$ is the interacting number of struts, and $n$ is the number of nodes in a lattice unit. The material exhibits bending-dominated
behavior under stress with relatively low strength when \( M < 0 \), and stretching-dominated behavior with high stiffness and strength when \( M > 0 \).

\[
M = s - 3n + 6 \quad (3)
\]

According to the Maxwell equation, to achieve a strong and stiff lattice structure, maximizing the number of struts joined at each node is desired. For this purpose, an octet-truss lattice structure was developed,\(^{191}\) and it shows linear relationships of \( E/E_s \) and \( \sigma/\sigma_s \) to \( \rho/\rho_s \).\(^{195-196}\) This indicates that the octet-truss lattice reaches the maximum value for \( C \) and the minimum value for \( n \) in the Gibson—Ashby equations, suggesting that it is the most efficient structural design for a lattice cellular material.

### 1.3.3 3-Dimensionally Ordered Macroporous (3DOM) Materials

Other than the materials mentioned in the last section, 3-dimensionally ordered macroporous (3DOM) materials have emerged as another promising structural material in recent years (Figure 1.4d).\(^{193, 197-200}\) 3DOM materials are a type of cellular material with highly ordered porous structure and are typically prepared through colloidal-crystal templating.\(^{201-203}\) In a typical synthetic route of 3DOM materials, a dispersion of monodisperse colloidal particles is assembled into close packed arrays that act as the colloidal-crystal template. A certain type of precursor is introduced into the voids of the template. The precursor is then converted into the desired 3DOM materials through heat treatment, during which the template is removed. The resulting 3DOM structure comprises solid material surrounding spherical voids, generally with face-centered cubic (FCC)
structure. Due to the flexibility of precursor choices in the synthesis, a wide variety of materials have been fabricated into 3DOM structures, such as polymers, C, SiO$_2$, TiO$_2$, V$_2$O$_5$, Ni, Cu, W, W-Mo, and many others.$^{193, 197, 200, 204-214}$

Several features of 3DOM materials make them interesting as a new type of structural material. The first one is their intrinsic nanometer-sized ligaments. Depending on the sizes of the templating colloidal crystals, the sizes of the pores in 3DOM materials can range from a few tens of nanometers to several micrometers.$^{215}$ Therefore, 3DOM materials are likely to exhibit extraordinary strength and stiffness without any further modification due to the nanosize effect.$^{168, 170-171, 216}$ The second one is its isotropic architecture, making them suitable for more applications than anisotropic structures, such as honeycomb structures. Another feature is that 3DOM materials have polyhedral cells with curved surfaces as their building units, not like lattices composed of struts connected by nodes. Therefore, Maxwell’s equation does not apply when one wants to calculate or predict the mechanical behaviors of 3DOM materials.

Do Rosário et al. studied the mechanical properties of a 3DOM SiO$_2$/TiO$_2$ material (3DOM silica coated with a TiO$_2$ thin layer) and found that it showed higher strength-to-weight ratios compared with an optimized alumina octet-truss lattice structure.$^{193, 199, 217}$ Additionally, the 3DOM SiO$_2$/TiO$_2$ material exhibited a relatively low density of 330—910 kg m$^{-3}$. Through finite element calculations, they found that the superior mechanical properties of 3DOM materials originated from their arc-like structures. This type of structure enables the applied stress on 3DOM materials to be dissipated well into the surrounding regions, therefore mitigating the stress concentration at the pore perimeter.
1.4 Development of Metal–Ceramic Nanocomposites

1.4.1 Introduction of Metal–Ceramic Nanocomposites

Advanced ceramic materials provide enhanced thermal stability, high hardness, and good chemical/oxidation resistance. They are attractive for many high performance applications in the automotive and aerospace industries, defense, and energy generation (fuel cells, thermoelectric generators, and nuclear reactors). A major challenge in the design and development of advanced ceramics is addressing their low toughness. Lacking a method of energy dissipation similar to that found in metals (plastic deformation), ceramics have poor flaw tolerance, making their failure unpredictable under high mechanical loads or in thermal-cyclic environments.

A breakthrough toward expanding the application range of ceramics was the development of metal–ceramic composites. The incorporation of metals into ceramics enhances the toughness and flaw tolerance of the overall materials through local plastic deformation and mechanical decoupling of the phases during fracture. This behavior enables them to survive a wider range of harsh conditions. Metal–matrix composites (MMCs) are a well-known and already commercialized metal–ceramic composite. In a metal–ceramic type of MMC, the reinforcing ceramic phase, usually as particles, whiskers, or fibers is dispersed in the metal matrix phase to enhance its certain properties. Another relatively new metal–ceramic composite is interpenetrating composite (IPC). Different from MMCs, IPCs consist of a co-continuous 3D interpenetrating network, in which each phase can be self-supporting if the other phase is imagined to be taken away. Therefore, IPCs feature 3D interconnected and intertwined structures instead of having discrete
reinforcing phases. One major advantage of IPCs is that they provide an opportunity for achieving the full functionality of different phases because they are all continuous throughout the structure.\textsuperscript{228-230} In addition, IPCs are good candidate materials when isotropic mechanical/physical properties are desired.\textsuperscript{218, 230-234} Compositions and applications of some developed metal–ceramic nanocomposites are shown in Table 1.2.\textsuperscript{218}

\textbf{Table 1.2.} Compositions and applications of some developed and currently commercialized ceramic-metal composites. Reprinted with permission from ref.\textsuperscript{218}, Copyright (2012), Taylor & Francis.

<table>
<thead>
<tr>
<th>application</th>
<th>composition</th>
<th>volume fraction of ceramic/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>cutting tools, dies, drills,</td>
<td>WC/Co, (TiC, MoSi\textsubscript{2})/Ni</td>
<td>60–90</td>
</tr>
<tr>
<td>jet blades</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wankel seals</td>
<td>TiC/Mo (W, Co), TiC/Fe</td>
<td>40–80</td>
</tr>
<tr>
<td>nuclear fuels</td>
<td>UO\textsubscript{2}/(U, Mo, W, Fe), PuO\textsubscript{2}/Fe</td>
<td>35–95</td>
</tr>
<tr>
<td>control rods</td>
<td>U\textsubscript{3}O\textsubscript{4}/Al, UA\textsubscript{12}/Al, B\textsubscript{4}C/Al</td>
<td>-</td>
</tr>
<tr>
<td>bearings</td>
<td>BN/W, Fe/Fe\textsubscript{2}O\textsubscript{3}</td>
<td>5–25</td>
</tr>
<tr>
<td></td>
<td>Fe/SiO\textsubscript{2}, Fe/SiO\textsubscript{2}/graphite, Fe/Al\textsubscript{2}O\textsubscript{3}/graphite</td>
<td>5–20</td>
</tr>
<tr>
<td>thermocouple protection</td>
<td>ZrO\textsubscript{2}/Mo, Al\textsubscript{2}O\textsubscript{3}/Mo, Cr\textsubscript{2}O\textsubscript{3}/Cr, Al\textsubscript{2}O\textsubscript{3}/W</td>
<td>25–40</td>
</tr>
<tr>
<td>crucibles</td>
<td>Al\textsubscript{2}O\textsubscript{3}/Fe</td>
<td>15</td>
</tr>
<tr>
<td>contacts</td>
<td>graphite/Cu (Sn, Pb), CdO/Ag, BeO/Cu</td>
<td>1–20</td>
</tr>
<tr>
<td>emitter cathodes</td>
<td>UO\textsubscript{2}/Mo, Ba\textsubscript{2}CaWO\textsubscript{3}/W</td>
<td>80–98</td>
</tr>
<tr>
<td>ignition pellets</td>
<td>Fe\textsubscript{2}O\textsubscript{3}/Al, BaO\textsubscript{2}/(Al, Mg), ThO\textsubscript{3}/Ca</td>
<td>70–80</td>
</tr>
<tr>
<td>armor</td>
<td>B\textsubscript{4}C/Al</td>
<td>65–80</td>
</tr>
</tbody>
</table>
1.4.2 Challenges for the Development of Metal–Ceramic Nanocomposites

Size effects have been observed in metal–ceramic composites. For metal–ceramic composites at nanometer-scale sizes, exceptionally high strength, toughness, and hardness can be achieved. The occurrence of these extraordinary properties of metal–ceramic nanocomposites has been attributed to several factors: (1) the presence of nanosized particles suppresses the formation of dislocations; (2) the component surrounding the nanoparticles generates compressive stress and creates a super modulus effect; (3) the components at the interfaces can exhibit exceptionally strong interactions.

Despite the potential of metal–ceramic nanocomposites to provide improved performance under extremes of stress and temperature, basic scientific questions still exist about how the nanostructures enhance the mechanical properties of the overall materials. Many studies have been carried out to understand the special mechanical behavior of nanosized structures. However, one major obstacle is the difficulty to achieve an even distribution of the reinforcing phases during the synthesis of metal–ceramic nanocomposites, which creates problems to correlate the properties of the fine structure with that of the overall materials. In this context, a careful structural design becomes the key to study the relationship between the nanoscopic structures and macroscopic mechanical properties of the metal–ceramic nanocomposites.

1.4.3 Development of Metal–Ceramic Nanocomposites Based on 3DOM Materials

Recently, the mechanical properties of 3DOM materials have drawn attention. As cellular materials with ordered and periodic architectures and nanosized ligaments, certain
compositions of 3DOM materials show interesting mechanical properties.\textsuperscript{184} For example, Pikul et. al. reported that 3DOM Ni exhibited a yield strength exceeding that of bulk Ni by more than 4 times.\textsuperscript{200} In addition, 3DOM materials have very low density due to their high porosity. When a certain 3DOM material is used as the scaffold, the other phase of the material can be introduced into the interconnected voids to form an IPC type nanocomposite. An even distribution of the embedded phase is achieved through this process due to the periodic nature of the 3DOM materials. By varying the combinations of the materials, enhanced mechanical properties, such as higher yield strength and better thermal stability are expected in the synthesized IPC nanocomposites.

1.5 Outline of the Remainder of the Dissertation

This dissertation focuses on the development of synthetic methods to fabricate different types of nanomaterials in which catalytic or mechanical properties can be modulated. The studied targets are mainly MOFs, 3DOM materials, and their derived nanocomposites. A main goal is to investigate the structure-property relationships of different materials at the nanometer scale. Another focus of this thesis is on characterizing the developed nanomaterials. The composition and structure of the developed nanomaterials are studied with multiple characterization methods.

Chapter 2 describes a study investigating how the phase purity and pore reinforcement affect the mechanical properties of MOF materials. The mechanical properties of MOF materials were not mentioned in this chapter but will be discussed in detail in Chapter 2. Briefly speaking, the structure–mechanical property relationships of MOFs are important
for their future commercialization. In Chapter 2, the mechanical properties of phase-pure NU-1000, NU-1000 containing MOF NU-901 as an impurity phase, and silica-reinforced phase-pure NU-1000 are investigated. By eliminating the impurity phase in NU-1000, its strength and stiffness are greatly enhanced, with the elastic modulus increased from 3 GPa to 21 GPa, and the yield stress raised from 300 MPa to 2.5 GPa. By reinforcing the pores of phase-pure NU-1000 with silica, its strength can be further improved, with the load at failure being increased from 2000 µN to 3000–4000 µN.

Chapters 3 and 4 describe the work of developing nanocomposites containing abundant and well-distributed sub-nanosized metal oxide clusters as potential catalysts through nanocasting MOF materials. In Chapter 3, a silica nanocasting method is developed to nanocast three cerium-based MOFs. Depending on the different structures of the MOFs, the aggregation of cerium clusters was mitigated to different degrees. Among the three products, nanocast (Ce)MOF-808 is very likely to retain the original oxocerium clusters from (Ce)MOF-808. The developed silica-oxocerium cluster nanohybrid material exhibits a high loading of cerium (51 wt%) with a good thermal stability at 750 °C. Additionally, the oxidation states of cerium in the nanohybrid can be varied reversibly between III and IV at 750 °C, indicating the potential of this material as a redox catalyst at high temperature.

Chapter 4 describes the work of developing a carbon-oxozirconium cluster nanohybrid material through nanocasting NU-1000 MOF. The developed carbon-based nanomaterial possesses the structure of isolated oxozirconium clusters distributed on a porous carbon scaffold. The product shows relatively high porosity (surface area >350 m²/g) and high
thermal stability for the clusters (no aggregation while being heated up to 800 °C in nitrogen). The electrical conductivity of the nanocast NU-1000 material is 0.41 S/m.

Chapters 5 and 6 focus on the mechanical properties of 3DOM materials and 3DOM material-derived nanocomposites. Chapter 5 describes the work of developing a convective self-assembly route to optimize the 3DOM tungsten (W) structure. Compared to the traditional sedimentation method used to prepare the colloidal crystal template, the 3DOM W material fabricated this way has larger domains of uncracked 3DOM regions with flat surfaces, making them good candidates for studying less defective microstructures. The resulting 3DOM W material has a periodic porous structure (with a low density of ~0.7–1.0 g/cm³, around 5% of the dense crystalline W) with a pore size of ~300 nm and nanocrystalline W ligaments with cross-sectional diameters of ~35–58 nm. The nanometer-sized W ligaments exhibit ~6× the yield strength of coarse-grained W, and ~2× the yield strength of 200-nm single-crystal W nanopillars. 241 The brittle-to-ductile transition temperature range of the 3DOM W is investigated. 242-246 It is demonstrated that the maximum strain of 3DOM W increases from 2.4% at room temperature (30 °C) to >20% above the brittle-to-ductile transition temperature (225 °C).

Chapter 6 describes the work of synthesizing a metal–ceramic nano-IPC material, 3DOM W–SiOC based on the 3DOM W material described in Chapter 5. In this nanocomposite, both the crystalline tungsten and amorphous silicon oxycarbide phases form continuous and interpenetrating networks, with some discrete free carbon nanodomains present. The W–SiOC material inherits the periodic structure from its 3DOM W matrix, and this periodic structure can be maintained up to 1000 °C. In situ SEM
micropillar compression tests demonstrate that the 3DOM W–SiOC material can sustain a maximum stress of 1.1 GPa, a factor of 22 greater than the 3DOM W matrix. Deforming behaviors of the developed 3DOM nanocomposite in a wide temperature range (30 °C to 575 °C) are investigated. The deformation mode of 3DOM W–SiOC exhibits a transition from fracture-dominated deformation at low temperature to plastic deformation above 425 °C.

The dissertation concludes with Chapter 7, which summarizes the innovations and contributions of this thesis work to the development of fabricating different types of nanocomposite materials, and their potential applications. Lastly, the author shares his opinions on possible directions of future work on functional nanomaterials.
Chapter 2

MOF Engineering: Enhancing the Mechanical Properties of NU-1000

Parts of this chapter were reprinted with permission from “Effects of Phase Purity and Pore Reinforcement on Mechanical Behavior of NU-1000 and Silica-Infiltrated NU-1000 Metal–Organic Frameworks” by Wang, Z.; Schmalbach, K. M.; Combs, R. L.; Chen, Y.; Penn, R. L.; Mara, N. A.; Stein, A. ACS Appl. Mater. Interfaces 2020, 12, 49971–49981

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This work was done in collaboration with Prof. Nathan Mara, Kevin M. Schmalbach, and Dr. Youxing Chen (performing nanoindentation and finite element analysis), Prof. R. Lee Penn and Rebecca L. Combs (synthesizing NU-1000, performing STEM-EDS, and collecting HAADF images) of University of Minnesota. The H₄TBAPy linker material for the NU-1000 synthesis was provided by Hupp and Farha group from Northwestern University. Prof. Antonia Antoniou, Dr. L. Chip Reisman, and Yuan Sheng contributed to this work by providing discussions regarding finite element modeling, carrying out TGA measurements, and carrying out ¹H NMR measurements, respectively.
2.1 Introduction

As discussed in Chapter 1, metal–organic frameworks (MOFs) have shown potential in many applications due to their unique structural and compositional features.\textsuperscript{82-88} However, for practical use and commercialization of MOFs, it may be necessary to densify and pelletize these high porosity, low density materials in processes that require high pressures. Therefore, in addition to their chemical properties, the mechanical properties of MOFs are another important criterion to assess whether a MOF is suitable for practical applications. Understanding the behavior of MOF materials under mechanical stress can facilitate the design and screening of robust MOFs for specific purposes. A few publications reported the influence of external pressure on certain chemical and structural properties of MOFs, such as phase transitions,\textsuperscript{247} bond breakage,\textsuperscript{248} and pore structure collapse.\textsuperscript{249-250} Additionally, Moghadam et al. studied the structure-mechanical property relationships for 3,385 MOFs using high-throughput molecular mechanics calculations.\textsuperscript{251} However, direct studies of the mechanical properties of MOFs remain challenging because many MOF materials consist of particles smaller than 1 μm, which makes them hard to manipulate and characterize by traditional mechanical testing methods.\textsuperscript{252-253} To date, studies on the mechanical properties of MOFs have been mainly performed on thin-film coatings and single crystals through traditional nanoindentation techniques.\textsuperscript{254-257} Recently, an atomic force microscopy (AFM)-based nanoindentation technique was applied to MOFs.\textsuperscript{258} With this method, mechanical data could be acquired for MOFs with even smaller particle sizes (< 500 nm).\textsuperscript{258} Elastic moduli and hardness values of some typical MOF materials are summarized in Table 2.1.
Table 2.1. Elastic modulus and hardness of some MOF materials determined by nanoindentation.a

<table>
<thead>
<tr>
<th>MOF</th>
<th>form</th>
<th>elastic modulus (GPa)</th>
<th>hardness (GPa)</th>
<th>indenter tip</th>
</tr>
</thead>
<tbody>
<tr>
<td>HKUST-1</td>
<td>thin film</td>
<td>9.3</td>
<td>0.23 ± 0.04</td>
<td>Berkovich</td>
</tr>
<tr>
<td></td>
<td>thin film</td>
<td>3.5 ± 2.5</td>
<td>0.17 ± 0.16</td>
<td>Berkovich</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>single crystal</td>
<td>3.2 ± 0.1</td>
<td>0.50 ± 0.02</td>
<td>Berkovich</td>
</tr>
<tr>
<td></td>
<td>single crystal</td>
<td>~3</td>
<td>~0.5</td>
<td>AFM-based</td>
</tr>
<tr>
<td>IRMOF-1</td>
<td>single crystal</td>
<td>2.7 ± 1.0</td>
<td>0.058 ± 0.026</td>
<td>Berkovich</td>
</tr>
<tr>
<td>UiO-66</td>
<td>nanoparticle</td>
<td>22–45</td>
<td>N.A.</td>
<td>AFM-based</td>
</tr>
<tr>
<td>UiO-67</td>
<td>single crystal</td>
<td>20.0</td>
<td>1.27</td>
<td>Berkovich</td>
</tr>
</tbody>
</table>

This table shows a selection of the most common MOF materials whose mechanical properties have been investigated. These properties can be modulated by manipulating the species of clusters and linkers. For example, when the zirconium atoms in the clusters of UiO-66 are substituted for hafnium, the elastic modulus increases from 22–45 to 30–60 GPa, because the Hf–O bond is stronger than the Zr–O bond. By incorporating more sterically bulky linkers, the elastic modulus of ZIF MOFs can be increased from 3 to 10 GPa.

Tan et al. reported a map of elastic modulus vs. hardness for major classes of materials, including metals, ceramics, polymers, and hybrid framework materials. From their results, MOFs mostly exhibit elastic moduli between 1–30 GPa and hardness values between 0.02–2 GPa. One interesting finding in their research is that the MOF region in the map overlaps with the intersection of regions for polymers, metals, and ceramics, indicating the potential of MOFs to substitute for traditional materials when specific
properties are preferred, such as ordered structure or large porosity. Notably, as organic–inorganic hybrid materials, MOFs do not have intrinsically high mechanical strength compared to other well-known porous materials consisting of inorganic building units. For example, the elastic moduli of silicalite-1 and ZSM-5 are 40 GPa and 57 GPa, respectively. Many other types of dense organic–inorganic hybrid materials can also outperform MOFs in terms of elastic modulus and hardness. For example, copper phosphonoacetate and cerium oxalate–formate hybrid materials show elastic moduli as high as 90 GPa and 78 GPa, respectively. However, MOFs have their unique structural advantages, including very low density, high surface area, uniform and ordered pores, all of which are attractive for many purposes. Therefore, elucidation of the mechanical properties of MOF materials is important for paving the way for their future commercialization.

The functionality of MOFs relies to a large extent on their open pore structures and unsaturated clusters. In other words, high porosity and low connectivity between clusters and linkers are desired for a MOF material to be competitive. However, these properties also result in low density and possibly lower stability, which compromise the mechanical properties of MOFs. One possible approach to address these competing tendencies is to introduce reinforcing components into the pores of MOFs while still leaving enough open space or maintaining the clusters unsaturated. To date, very few papers have been published regarding this topic.

Robison et al. reported a method to enhance the bulk modulus of NU-901 at the expense of increasing the connectivity of the clusters from 8 to 10 (still leaving 2 unsaturated sites
for each cluster). Malonzo et al. and Zhao et al. reported the partial filling of the pores of NU-1000 with amorphous silica, titania, or polymer, which maintained 48–77% of its original porosity. However, the mechanical properties were not studied after introducing the reinforcing phases.

NU-1000 is a relatively thermally stable, mesoporous MOF, which consists of oxo-zirconium clusters ("Zr_6" clusters, \([\text{Zr}_6(\mu_3-\text{O})_4(\mu_3-\text{OH})_4(\text{OH}_2)_4]^{8+}\)) and 1,3,6,8-tetrakis\((p\text{-benzoate})\)pyrene (TBAPy\(^{4+}\)) linkers (Figure 2.1). In a Zr_6 cluster, the six Zr atoms are aligned in the shape of octahedron with each triangular face capped with \(\mu_3\)-O or \(\mu_3\)-OH groups. This rigid structure with high symmetry endows NU-1000 with superior chemical and thermal stabilities compared to many other MOFs. Another advantage of NU-1000 is the unsaturated nature of the Zr_6 clusters, in which only eight out of the twelve edges in the Zr_6-octahedron are connected with linkers. The unoccupied sites in the Zr_6 clusters make NU-1000 a good substrate for further modifications, which extends its application range in catalysis, CO\(_2\) adsorption, and remediation of toxins.
Figure 2.1. Structures of NU-1000, Zr$_6$ cluster, and H$_4$TBAPy linker. In NU-1000, each Zr$_6$ cluster is connected to eight linkers and each linker is connected to four Zr$_6$ clusters.

In earlier studies of NU-1000, another phase, NU-901 was typically present as an impurity at a fraction of ~20% on the basis of a single-crystal X-ray diffraction analysis. NU-1000 and NU-901 are both composed of Zr$_6$ clusters with 8-fold connectivity by the TBAPy$^4^-$ linkers. However, their structures differ topologically. The Zr$_6$ clusters in NU-1000 are aligned at an angle of 60° relative to each other, whereas they are positioned parallel to each other in NU-901. This topology change reduces the largest pore size from 3.1 nm in NU-1000 to 1.2 nm in NU-901 and increases the density of the MOF. The
presence of an NU-901 impurity also alters the morphology of NU-1000 particles and can result in twinning. The NU-901 phase is typically present at mid-length of the NU-1000 particles.\textsuperscript{272} The key for the achievement of phase-pure MOFs was later found to be the use of appropriate modulators.\textsuperscript{271-273} Modulators are molecules that usually have the same functional group as the linkers but only on one side (monodentates). They adjust the reaction kinetics via capping the clusters at the beginning and slowly releasing them to connect with the linkers. The equilibrium between the modulator-capped clusters and linkers regulates the MOF crystal growth.\textsuperscript{274} The inclusion of an NU-901 phase can be inhibited by replacing benzoic acid as a modulator by larger biphenyl-4-carboxylic acid molecules, which causes stronger steric interactions between the capped metal clusters during their assembly.\textsuperscript{272} As a result, the rotation of the C–C bond and Zr\textsubscript{6} clusters is prevented, avoiding the formation of the NU-901 phase (Figure 2.2).
Figure 2.2. Structures of (a) NU-1000 and (b) NU-901. Both MOFs are composed of $\text{Zr}_6$ clusters and TBAPy$^+$ linkers. However, the clusters in NU-1000 are aligned at 60° relatively to each other whereas in NU-901 all clusters are aligned in parallel. In addition, NU-1000 has two types of pores (3.1 nm and 1.1 nm), but NU-901 only has one type (1.2 nm). Color code: Zr (blue); O (red); C (grey); H (white). (c) Scheme showing the formation of NU-901 inside NU-1000 using benzoic acid as the modulator and the prevention of NU-901 forming with biphenyl-4-carboxylic acid as the modulator. Part (c) was adapted with permission from ref.272, Copyright (2017), American Chemical Society.

Here we compare the effects of phase purity and an internal reinforcing phase on mechanical properties of NU-1000 by nanoindentation and finite-element simulation. Three types of NU-1000 single crystals were compared: phase-pure NU-1000 prepared with biphenyl-4-carboxylic acid as a modulator (NU-1000-bip), NU-1000 prepared with benzoic acid as a modulator (NU-1000-ben), which results in an additional, denser impurity
phase of NU-901, and NU-1000-bip whose mesopores were infiltrated with silica (SiO$_x$(OH)$_y$@NU-1000) by nanocasting methods. These last materials have previously been applied to provide thermal stabilization for Zr$_6$ clusters for high-temperature applications.\textsuperscript{135, 141, 146-147} This comparison provides insight into the effects of non-intentional and intentional secondary phases on the mechanical properties of NU-1000.

2.2 Experimental

2.2.1 Materials

Chemicals used in this study were obtained from the following sources: 1,3,6,8-tetrakis($p$-benzoic acid)pyrene (H$_4$TBAPy) synthesized by the Hupp and Farha groups at Northwestern University via a previously reported method;\textsuperscript{116} ethanol (anhydrous, 200 proof) from Pharmco-AAPER; $N$,$N$-diethylformamide (DEF, certified ACS, 99.9%), acetone (certified ACS, 99.7%) from Fisher Chemical; tetramethyl orthosilicate (98%), methanol (>99.8%), hydrochloric acid (ACS reagent, 37%), zirconium(IV) chloride (≥ 99.9%) from Sigma-Aldrich; biphenyl-4-carboxylic acid (98%) from Alfa Aesar; sodium hydroxide (99%) from Riedel-de Haën. Deionized water was used in all syntheses after purification to a minimum resistivity of 18.2 MΩ·cm with a Milli-Q PLUS reagent-grade water system.

2.2.2 Synthesis of NU-1000

Two types of NU-1000 were used in this study, each synthesized with a different modulator. The NU-1000 synthesized using benzoic acid as modulator was denoted as NU-
1000-ben. The synthesis of NU-1000-ben followed a previously reported method. The NU-1000 synthesized using biphenyl-4-carboxylic acid was denoted as NU-1000-bip. NU-1000-bip was synthesized as follows. Biphenyl-4-carboxylic acid (6.343 g, 32.00 mmol) and ZrCl₄ (139.8 mg, 0.60 mmol) were added into 16 mL of N,N-diethylformamide (DEF) and heated at 100 °C for 1 h. The Zr₆ clusters capped with biphenyl-4-carboxylic acid were obtained in this process. To prepare the linker suspension, H₄TBAPy acid (100 mg, 0.15 mmol) was suspended in 1.5 mL of DEF using sonication for better dispersion. An amount of 14.6 µL (0.015 mmol) of 1 M NaOH was then added to the linker suspension. The linker suspension was finally added to the suspension of the Zr₆ clusters. The mixture was heated at 100 °C for 48 h and then cooled down to room temperature. It was centrifuged at 9,000 rpm for 10 min, the supernatant was discarded, and the precipitate was dissolved with fresh DEF. This washing step was repeated twice. After the final washing step, the precipitate was suspended in 16 mL of fresh DEF. This suspension was mixed with 1 mL of 8 M HCl solution, which was then heated at 80 °C for 20 h. The reaction mixture was cooled to room temperature and centrifuged at 9,000 rpm for 10 min. The precipitate was washed three times with DEF and three times with acetone. Particles were left to dry overnight under air. This synthesis produced particles with lengths up to 10 µm. When the amounts of all synthesis components were cut in half, particles with lengths up to 2.5 µm were formed. The phase-pure NU-1000 is denoted as NU-1000-bip in the following text. Composition of NU-1000-ben: Zr₁₀C₁₄₆H₁₁₄O₅₇, composition of NU-1000-bip: Zr₁₀C₁₃₆H₁₁₃O₅₄, theoretical composition for both: Zr₁₀C₁₄₇H₁₀₀O₅₃. The synthesis of NU-1000-bip was performed by Rebecca L. Combs from the Penn group, Department of Chemistry, UMN.
2.2.3 Synthesis of SiO\textsubscript{x}(OH)\textsubscript{y}@NU-1000

Silica-infiltrated NU-1000 was synthesized following a published method.\textsuperscript{135} Volumes of 100 \(\mu\)L of deionized water and 180 \(\mu\)L of methanol were added into 600 \(\mu\)L of tetramethyl orthosilicate (TMOS). The mixture was sonicated for 10 min and then added to 30 mg of activated NU-1000. The infiltration of TMOS into NU-1000 was allowed to proceed for 24 h hours for batches with particle sizes up to 2.5 \(\mu\)m and 40, 80 or 100 h for batches with particle sizes up to 10 \(\mu\)m. The infiltrated MOF was then washed twice with methanol to remove any TMOS remaining on the external surface of the NU-1000 particles. The mixture was heated at 50 °C for 5 min to dry, and then exposed to HCl vapor for 24 h at room temperature in order to induce the condensation of TMOS. The mixture was then heated at 80 °C for 24 h. The resulting product was denoted as SiO\textsubscript{x}(OH)\textsubscript{y}@NU-1000.

2.2.4 Preparation of Segregated Dispersed Particles for Mechanical Testing

A spatula tip of NU-1000 or SiO\textsubscript{x}(OH)\textsubscript{y}@NU-1000 particles was dispersed in 2 mL of acetone. The mixture was sonicated for 10 min. One drop of the dispersion was added onto a silicon wafer (0.5 cm × 0.5 cm). After the acetone evaporated, isolated individual particles were present on the silicon wafer. The silicon wafer was then attached to an SEM stub with Super Glue.
2.2.5 Characterization

FT-IR spectra were obtained in transmission mode using a Nicolet Magna 760 IR spectrometer, using powdered samples compressed between a pair of NaCl windows. Powder X-ray diffraction patterns were collected using a PANalytical X’Pert Pro diffractometer. The X-rays were generated with a Co anode (Kα radiation, λ = 1.789 Å) operating at 45 kV accelerating voltage, 40 mA emission current. 1H nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Ascend AV-500 spectrometer at room temperature. Nitrogen sorption experiments were performed on a Quantachrome Autosorb-iQ2 analyzer using ultrahigh purity grade nitrogen adsorptive. All samples were degassed under dynamic vacuum (0.003 mTorr) at 120 °C for 12 h before analyses. Brunauer–Emmett–Teller (BET) surface areas were evaluated from the adsorption isotherms in the relative pressure range 0.01–0.20. Scanning electron microscopy (SEM) was performed on a JEOL-6500 field emission scanning electron microscope with an accelerating voltage of 5.0 kV. Scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM-EDS) was conducted using a JEOL JXA-8900 electron probe microanalyzer equipped with an Ultradry-SDD detector and operating with an accelerating voltage of 15.0 kV to 20 kV. All samples were coated with a 50 Å platinum film prior to SEM imaging or a 70 Å carbon film for EDS analyses. Transmission electron microscopy (TEM) measurements were obtained using a FEI Tecnai T12 transmission electron microscope with an accelerating voltage of 120 kV and a LaB₆ filament. Samples were sonicated for 5 min in ethanol and then deposited onto carbon film-coated copper grids. Scanning transmission electron microscopy–energy dispersive X-ray spectroscopy
(STEM-EDS) was performed using an FEI Tecnai G2 field-emission S/TEM operating at an accelerating voltage of 80 kV. Samples were loaded onto 300-mesh lacey carbon/Cu TEM grids by drop-casting a dilute suspension of each sample in acetone. High-angle annular dark field (HAADF) images were collected on an E. A. Fischione annular detector using an inner collection semi-angle of 25.5 mrad. Energy-dispersive X-ray spectroscopy (EDS) spectra were obtained using the ChemiSTEM EDX spectrometer. EDS maps were collected while rastering the beam over the sample, which minimized beam damage. A probe current of ~0.8 nA was used, and maps were collected over a minimum of 5 min. Data were analyzed using ESPRIT software (version 1.9.4). Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 TGA in air with a heating rate of 5 °C/min to estimate the Zr content in the samples from the residual mass (ZrO₂). The analyses of carbon and hydrogen content in the samples were carried out by Atlantic Microlab, Norcross, GA. The HAADF images and EDS spectra were collected by Rebecca L. Combs from the Penn group, Department of Chemistry, UMN.

2.2.6 Nanoindentation

The mounted sample was placed in a Hysitron PI88 in situ nanoindenter (Bruker Nano Surfaces, Minneapolis, MN) equipped with an xR low load transducer and a 20 μm diameter diamond flat punch probe. A minimum of three in situ compression experiments were conducted in an FEI Helios G4 UX FIB/SEM (Thermo Fisher Scientific) operated at 2 kV. The indenter was operated in displacement control mode with a displacement rate of 15 nm/s.
2.2.7 Finite Element Analysis

Compression along the flat face of the hexagonal cross section of the particles produces a non-uniform stress state in the particle. To quantify the average properties in the cross section, finite element modeling was performed using Abaqus/Standard (Dassault Systems). A two-dimensional regular hexagonal planar cross section (height of 1 µm for NU-1000-bip, height of 2 µm for NU-1000-ben) was compressed using CPS3 plane stress nodes. Only the initial loading of the MOF particles was modeled to approximate the elastic properties. These models assumed a dense, elastically isotropic material. The elastic modulus input was varied to produce load–displacement curves for the elastic region of the loading. This part and the nanoindentation were performed by Kevin M. Schmalbach from the Mara group, Department of Chemical Engineering and Materials Science, UMN. More detail can be found in our published paper.275

2.3 Results and Discussion

2.3.1 Structure and Composition of NU-1000 and SiO$_x$(OH)$_y$@NU-1000

Whereas NU-1000-ben contains NU-901 as an impurity phase, this impurity was eliminated in NU-1000-bip by changing the modulator from benzoic acid to biphenyl-4-carboxylic acid during the synthesis. The structural differences between these two materials were previously reported.272 Structural and compositional properties of the NU-1000-ben and NU-1000-bip materials used here were characterized by multiple methods, including SEM, N$_2$ sorption, XRD, TGA and CHN analysis.
The morphology of NU-1000 particles changed as the impurity phase was removed. Webber et al. had previously shown that NU-1000-ben was denser near the middle of the particles, which resulted in TEM phase contrast that was not seen in NU-1000-bip (Figure 2.3a, b). Here, SEM images revealed that NU-1000-ben crystals are narrower at mid-length and usually display twinning on the external surface of the rods, whereas phase-pure NU-1000 crystals have a straight rod shape with a hexagonal cross-section and smoother surfaces (Figure 2.3c, d).
Figure 2.3. TEM images and SEM images of NU-1000-ben particles with an NU-901 impurity phase (a), (c) and phase-pure NU-1000-bip particles (b), (d). The denser impurity phase NU-901 is located near the centers of NU-1000-ben particles (a), resulting in higher phase contrast in those regions. The presence of NU-901 also alters the morphology of the NU-1000 particles, which results in a narrower center part (c). Phase-pure NU-1000 particles are more uniform in density (b) and exhibit straight rod shapes with smoother surfaces (d). The different modulators and schemes showing the formation of NU-901 and NU-1000 are shown as insets in (a) and (b). Figures (a) and (b) are reprinted with permission from ref. 272, Copyright 2017, American Chemical Society.
NU-1000-ben and NU-1000-bip both exhibited high surface areas and porosity (Figure 2.4a, Table 2.2). Although the powder XRD patterns of these samples in the low-angle region (Figure 2.4b) could not distinguish between the NU-1000 and NU-901 phases, the N\textsubscript{2} sorption isotherms showed clear differences in the micropore and mesopore regions. The isotherm for NU-1000-bip showed the features of both micropores (relative pressure $P/P_0 < 0.1$) and mesopores ($P/P_0 > 0.5$), which are also apparent in the pore size distribution curve (Figure 2.4a inset). The peak at 1.2 nm corresponds to the smaller, triangular micropores and the peak at 2.7 nm corresponds to the larger hexagonal mesopores (see Figure 2.2). The isotherm for NU-1000-ben indicates a greater N\textsubscript{2} volume adsorbed at low relative pressure and a slightly lower volume at high relative pressure; in addition, the peak at 2.7 nm is reduced in intensity compared to that at 1.2 nm. Compared to NU-1000-bip, NU-1000-ben contains a larger fraction of micropores due to the NU-901 impurity phase, which only has micropores. On the basis of the change in micropore fraction, the fraction of NU-901 in NU-1000-ben was estimated to be about 20%, consistent with the value reported from single crystal analysis (Table 2.2).\textsuperscript{35}
Figure 2.4. (a) N$_2$ sorption isotherms of NU-1000-bip and NU-1000-ben samples (DFT pore size distribution as the inset). Pore size distributions were calculated by NLDFT using a slit pore model. (b) XRD patterns of NU-1000-bip, NU-1000-ben, simulated NU-1000, and simulated NU-901.
Table 2.2. Surface area, micropore volume, mesopore volume and total pore volume of NU-1000-ben and NU-1000-bip samples.

<table>
<thead>
<tr>
<th>MOF</th>
<th>surface area (m² g⁻¹)</th>
<th>micropore volume (cm³ g⁻¹)</th>
<th>mesopore volume (cm³ g⁻¹)</th>
<th>total pore volume (cm³ g⁻¹)</th>
<th>micropore percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NU-1000-ben²</td>
<td>2577</td>
<td>0.69</td>
<td>0.76</td>
<td>1.45</td>
<td>48</td>
</tr>
<tr>
<td>NU-1000-bip</td>
<td>2497</td>
<td>0.60</td>
<td>0.94</td>
<td>1.54</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>(batch 1, Fig. 2.4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NU-1000-bip</td>
<td>1905</td>
<td>0.45</td>
<td>0.74</td>
<td>1.19</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>(batch 2, Fig. 2.6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiOₓ(OH)ᵧ@NU-1000-bip (from batch 2)</td>
<td>1292</td>
<td>0.35</td>
<td>0.38</td>
<td>0.73</td>
<td>48</td>
</tr>
</tbody>
</table>

Notes: ¹ Batch 1 was used for mechanical testing. Batch 2 was used for additional structural and compositional characterization.

² The fraction of NU-901 in NU-1000-ben, x, was estimated to be about 20% by comparison with the micropore volume fraction for NU-901 of 87% reported in ref.²⁷⁶ and using the average micropore fractions for NU-1000-bip for batches 1 and 2: (1–x)(0.385) + x(0.87) = 0.48.

Because MOF materials are highly porous, it was hypothesized that with extra reinforcing material introduced into their pores, the overall mechanical properties of the material could be enhanced. The feasibility of introducing different materials into the pores
of MOFs has been reported elsewhere. In this study, TMOS was introduced into the pores of NU-1000 after extensive washing with DEF and acetone, which ensured that either benzoic acid or biphenyl-4-carboxylic acid modulators were almost completely removed from the MOF particles (Figure 2.5). This was followed by hydrolysis and condensation of TMOS by exposing the infiltrated particles to HCl vapor. The infiltration of TMOS into the pores was facilitated by capillary forces (NU-1000 was preheated under vacuum to evacuate the air and water from the pores). After the infiltration process, the material was washed with methanol to remove any remaining TMOS from the external surface of the NU-1000 particles. Because the materials were dried at a relatively low temperature of 60 °C, the embedded silica still contained a large fraction of hydroxyl groups. Therefore, the reinforcing material formed inside the pores was denoted as SiO$_x$(OH)$_y$, and the whole material was denoted as SiO$_x$(OH)$_y$@NU-1000. To focus on the role of the reinforcing phase on mechanical properties without influence from any NU-901 phase impurity, the introduction of SiO$_x$(OH)$_y$ was only performed on NU-1000-bip in this study.
Figure 2.5. $^1$H NMR spectra of NU-1000-ben, NU-1000-bip, and bip (biphenyl-4-carboxylic acid) and ben (benzoic acid) as reference samples. NU-1000-ben and NU-1000-bip were first digested to prepare solutions for the NMR measurements. The digestion process was carried out as follows: 8 drops of D$_2$SO$_4$ were added into a scintillation vial containing 2 mg of the NU-1000 samples. The vial was capped and heated at 75 °C until the mixture became homogeneous. 1 mL DMSO-d$_6$ was then added, and a yellow solution was obtained. The control samples were also processed in the same way to prepare the NMR solution. Peaks labeled with (+) are from the TBAPy$^+$ linkers. These data confirmed that the modulators had been almost completely removed from the MOF particles after the washing procedure with DEF and acetone.

Structural details of SiO$_x$(OH)$_y$@NU-1000-ben were reported in a previous publication (the structure was referred to as SiO$_2$@NU-1000). It was observed that after the
infiltration of silica into NU-1000-ben, the specific surface area, pore volume, and pore diameter decreased (from 2064 to 901 m$^2$/g, 1.44 to 0.55 cm$^3$/g, and 2.7 to 2.2 nm, respectively), indicating the presence of silica inside the pores of NU-1000-ben. In addition, silica was found to occupy mainly the 3.1 nm mesopores on the basis of gas sorption and difference envelope density analyses.

The textural characteristics of the SiO$_x$(OH)$_y$@NU-1000-bip system were similar to those observed for SiO$_x$(OH)$_y$@NU-1000-ben, confirming the incorporation of silica in the pores of NU-1000-bip (Figure 2.6, Table 2.2). After infiltration with silica, the specific surface area of NU-1000-bip decreased from 1905 to 1292 m$^2$/g and the pore volume from 1.19 to 0.73 cm$^3$/g (Table 2.2). The pore size distribution curve calculated from N$_2$ sorption measurements (Figure 2.6b) showed a significant decrease in intensity for the larger mesopores with a shift from 2.7 to 2.3 nm, while the peak at 1.2 nm corresponding to the small micropores maintained its position. These results indicated that the introduced silica mainly occupied the larger mesopores, similar to what was reported for SiO$_x$(OH)$_y$@NU-1000-ben.
Figure 2.6. (a) N\textsubscript{2} sorption isotherms and (b) DFT pore size distributions of NU-1000-bip and SiO\textsubscript{x}(OH)\textsubscript{y}@NU-1000-bip samples. Pore size distributions were calculated by NLDFT using a slit pore model.

Changes in the XRD patterns after NU-1000-bip was infiltrated with silica (Figure 2.7) also paralleled observations for SiO\textsubscript{x}(OH)\textsubscript{y}@NU-1000-ben. Major peaks of NU-1000 were
still observed after the infiltration except for the (100) peak at 3°. The (100) planes in NU-1000 cut through the larger hexagonal mesopores and the decreased intensity of this peak for the SiO$_x$(OH)$_y$@NU-1000-bip sample results from the reduction in electron contrast as the hexagonal pores are partially filled with silica. Other peaks are broadened after infiltration of NU-1000-bip with silica.

Figure 2.7. XRD patterns of NU-1000-bip and SiO$_x$(OH)$_y$@NU-1000-bip materials. The inset illustrates the (100) plane in NU-1000.

In contrast, the distribution of silica throughout individual SiO$_x$(OH)$_y$@NU-1000-bip and SiO$_x$(OH)$_y$@NU-1000-ben particles differed, as revealed by STEM-EDS maps. While Si was distributed uniformly throughout SiO$_x$(OH)$_y$@NU-1000-bip particles (Figure 2.8),
the Si concentration near the middle of SiO₃(OH)ₓ@NU-1000-ben particles typically deviated from the remaining areas of the particles. This behavior supported the location of the NU-901 phase impurity in SiO₃(OH)ₓ@NU-1000-ben and the absence of such an impurity in SiO₃(OH)ₓ@NU-1000-bip. No external silica crust was observed in either sample.
Figure 2.8. Representative high-angle annular dark-field images and energy-dispersive X-ray spectroscopy maps of (a) SiO$_x$(OH)$_y$@NU-1000-ben particles and (b) SiO$_x$(OH)$_y$@NU-1000-bip particles. All particles are completely infiltrated with silica and no external silica crust is visible. In the case of the SiO$_x$(OH)$_y$@NU-1000-ben particles, the Si and Zr concentrations change near the middle of particles, as pointed out by the white arrows. This coincides with the proposed region for the NU-901 impurity in these particles. The more uniform distribution of Si and Zr in SiO$_x$(OH)$_y$@NU-1000-bip particles supports the absence of such an impurity phase.

For mechanical testing, we aimed to use the largest possible particles of NU-1000-bip and SiO$_x$(OH)$_y$@NU-1000-bip. For NU-1000 particles up to 2.5 µm in length, an infiltration time of 24 h was suitable to achieve efficient infiltration with a silica scaffold.$^{135}$
However, in the present study, for the application of the silica infiltration method to the more defect-free NU-1000-bip material, the influence of infiltration time on composite structure was re-evaluated, considering the facts that: (1) unlike NU-1000-ben, NU-1000-bip contains purely the NU-1000 phase, so the fraction of 3.1 nm pores is larger; and (2) larger NU-1000 particles (~10 µm in length) would be expected to require a longer time for diffusion of TMOS through the particle. Three different infiltration times were investigated: 40, 80, and 100 h, and the extent of infiltration was evaluated by comparing characteristic FT-IR absorptions of silica to those of NU-1000 (Figure 2.9).
Figure 2.9. (a) FT-IR spectra of NU-1000-bip and a series of SiO\textsubscript{x}(OH)\textsubscript{y}@NU-1000-bip materials prepared using different infiltration times. (b) Zoomed-in FTIR spectra of a series of SiO\textsubscript{x}(OH)\textsubscript{y}@NU-1000-bip samples. No peaks were observed in the 963–980 cm\textsuperscript{-1} range.

In the FT-IR spectra, peaks at 1417 and 1100 cm\textsuperscript{-1} correspond to the asymmetric vibration of COO\textsuperscript{−} and stretching vibrations of Si–O–Si, respectively. The COO\textsuperscript{−} peak is representative of the presence of TBAPy\textsuperscript{4+} linkers, and Si–O–Si indicates the presence of silica. Because the number of linkers did not change during the infiltration process, the peak area ratio of \( \nu_{\text{Si-O-Si}} / \nu_{\text{COO}} \) is an indication of the relative content of silica in SiO\textsubscript{x}(OH)\textsubscript{y}@NU-1000-bip. These ratios were 1.4, 1.6, and 1.7 for samples infiltrated for 40, 80, and 100 h, indicating that more silica was introduced with longer infiltration time. This result was consistent with SEM-EDS data, which revealed increasing Si/Zr\textsubscript{6} ratios.
from 23, 29, and 34 for the NU-1000-bip samples infiltrated with TMOS for 40 h, 80 h, and 100 h. In a previous study of infiltrating smaller particles of modified NU-1000 with silica, the Si/Zr ratio surpassed 50. Therefore, the Si/Zr ratio in this study might be further increased with infiltration times longer than 100 h. The SiO₄(OH)₄@NU-1000-bip-100h material which contained the largest amount of silica was selected for mechanical testing, considering that it should show the greatest impact of the secondary phase on mechanical properties.

At this point it is not known how the silica interacts with the Zr₆ clusters. A possible binding site for silica in NU-1000 would be the –OH groups on the zirconium oxide clusters to form Si–O–Zr bonds. Corresponding Si–O–Zr vibrations would exhibit IR signals in the 963–980 cm⁻¹ range. In addition, Chen et al. observed that the Si–O–Si IR peak shifted to a lower wavenumber in a Cr₂O₃/SiO₂ (28 wt% SiO₂) composite compared to SiO₂, due to the formation of Si–O–Cr bonding. Therefore, one might expect to see as well the Si–O–Si IR peak shift in SiO₄(OH)₄@NU-1000-bip if there is Si–O–Zr bonding. However, no IR peaks appeared (in 963–980 cm⁻¹) or shifted (1100 cm⁻¹ peak) for SiO₄(OH)₄@NU-1000-bip (Figure 2.9). However, given the relatively high Si:Zr ratio in these materials, the possibility of silica–Zr₆ cluster interactions cannot be excluded.

SEM images confirmed that the morphology of NU-1000-bip was maintained even after long infiltration with TMOS in the SiO₄(OH)₄@NU-1000-bip-100h particles (Figure 2.10). Rod-shaped particles were still observed with no evidence for any extraneous silica particles formed on the outside if the infiltrated particles, which was ensured by the washing process to remove any remaining TMOS after the infiltration process. Further
evidence for the absence of an external silica layer around the NU-1000 was provided by contrast analysis of a TEM image of SiO$_x$(OH)$_y$@NU-1000-bip-100h (**Figure 2.10c**).

**Figure 2.10.** SEM images of (a) NU-1000-bip and (b) SiO$_x$(OH)$_y$@NU-1000-bip-100h. (c) TEM image of SiO$_x$(OH)$_y$@NU-1000-bip-100h.

To investigate the mechanical properties of the NU-1000 and the SiO$_x$(OH)$_y$@NU-1000 particles, it is important to keep them separated as single particles in order to prevent particle stacking which would complicate the mechanical analysis. To obtain highly dispersed particles on a substrate, small amounts of NU-1000 or SiO$_x$(OH)$_y$@NU-1000 materials were dispersed in acetone. After sonication, the dispersion was dropped onto silicon wafers. Separate, well-dispersed particles were left on the silicon substrate after the acetone evaporated (**Figure 2.11**). The average dimensions (length/width) of the particles were measured to be 9.5 ± 0.5 μm/ 2.3 ± 0.3 μm for NU-1000-ben, 10.5 ± 2.0 μm/ 1.1 ± 0.2 μm for NU-1000-bip, and 10.8 ± 1.8 μm/ 1.1 ± 0.2 μm for SiO$_x$(OH)$_y$@NU-1000-bip-100h (6 separate rods were measured for each sample).
2.3.2 Mechanical Testing of NU-1000 and SiO$_x$(OH)$_y$@NU-1000

NU-1000 and SiO$_x$(OH)$_y$@NU-1000-bip particles were compressed under the indenter. The height of the particles decreased from 1.2 to 0.5 μm for NU-1000-bip, 1.1 to 0.5 μm for SiO$_x$(OH)$_y$@NU-1000-bip-100h, and 2.0 to 1.2 μm for NU-1000-ben (Figure 2.12). None of the three particles fractured under compression, implying their good fracture resistance in the direction parallel to the hexagonal cross-section.

Figure 2.11. SEM images of (a) NU-1000-ben, (b) NU-1000-bip, and (c) SiO$_x$(OH)$_y$@NU-1000-bip-100h particles.
Figure 2.12. SEM images of NU-1000-bip, SiO$_2$(OH)$_x$@NU-1000-bip-100h, and NU-1000-ben particles before compression (a, c, e) and after compression (b, d, f) under the indenter. Small extraneous particles seen around the indented particle in (f) were also present on the precursor sample in (e). They were not identified and are not believed to influence the measurements. The scale bar in all images corresponds to 2 μm.

On the basis of the compressive load—displacement curves (Figure 2.13a), one can compare several important mechanical properties of the three types of materials, including their loading stiffness (slope of the linear part of the curve) and the load at failure (the load at the deviation point from the linearity). NU-1000-bip and silica-infiltrated NU-1000-bip exhibited similar loading stiffness, which significantly exceeded that of NU-1000-ben. This result suggested that the phase purity and structure integrity are important for a MOF particle to be robust.

In terms of load at failure, it is likely related to the collapse of the pore structure. In other words, a MOF structure exhibiting higher load at failure is stronger and can possibly endure higher stress before deforming and losing the pore structure. The phase-pure NU-
1000-bip fails at around 2000 µN, a value approximately 4 times higher than for the phase-impure NU-1000-ben. After the MOF was reinforced with silica in the pore, the load at failure of SiO$_x$(OH)$_y$@NU-1000-bip was further increased by 50–100% to 3000–4000 µN. The difference between NU-1000-bip and silica-infiltrated NU-1000-bip indicated that the silica inside the pores could carry some load beyond a certain load applied, strengthening the material to be elastically deformed at a higher load.
Figure 2.13. (a) Load–displacement curves for the compression of NU-1000-bip (red), NU-1000-ben (blue), and SiO$_x$(OH)$_y$@NU-1000-bip (black). NU-1000-bip and SiO$_x$(OH)$_y$@NU-1000-bip have significantly higher stiffness than NU-1000-ben. (b) Load–displacement curves from (a) plotted on a smaller scale.
Overlaid are the simulated load–displacement curves from finite element modeling (FEM) assuming elastic moduli (E) of 20 GPa (purple) and 3 GPa (green). (c) Load–displacement curves from (b) incorporating an elastic–perfectly plastic solution using a yield stress, \(\sigma_y\), of 2.5 GPa for NU-1000-bip and 300 MPa for NU-1000-ben. In a linear elastic material, the initial load–displacement response is expected to be linear for a linear elastic material. After the linear loading response, a deviation from linearity typically indicates some type of permanent deformation, such as plastic deformation or fracture. The point of deviation from linearity is considered the point of failure.

### 2.3.3 Finite Element Simulation

To quantify the effective elastic modulus of NU-1000 and silica-infiltrated NU-1000 materials, the loading of a hexagonal planar section of material was simulated using Abaqus/Standard. In the simulation, an elastic-plastic model was applied, where the material first underwent elastic deformation and began to yield once the material reached its yield stress. The load–displacement output of the simulation is overlaid on the experimental load–displacement curves (Figure 2.13b and c). Based on the simulated results of the elastic region (Figure 2.13b), the elastic modulus for NU-1000-ben, NU-1000-bip, and silica-infiltrated NU-1000-bip were estimated to be 3.2 ± 0.7 GPa, 21 ± 3.7 GPa, and 19 ± 3.9 GPa, respectively.

In addition to determining the elastic moduli of the particles, the simulations also helped elucidate the distribution of stress within the particles at the point of load failure (Figure 2.14). High stresses were observed at the top and bottom vertices of the hexagon. However, the stresses were very low toward the other vertices which were not under direct loading. More importantly, the stresses were not limited merely to the volume between the
top and bottom vertices, but they exhibited some lateral spread. At the point of failure in NU-1000-bip, the von Mises stress within the bulk of the particle was on the order of 2.5 GPa, whereas it was much lower for NU-1000-ben, on the order of 300 MPa.

Figure 2.14. (a) The shape of the stress distribution at the point of failure assuming isotropic elasticity. Colors correspond to stress contours for (b) NU-1000-bip and (c) NU-1000-ben. Stresses are von Mises stresses with units of TPa. The bulk stress at failure is approximately 2.5 GPa for NU-1000-bip and 300 MPa for NU-1000-ben. The von Mises stress is a number value calculated on the basis of the different stress tensors applied on the structure. A map of stress distribution could be derived then according to the calculated von Mises stress.

In terms of the plastic region, which corresponds to the post-failure part on the load–displacement curve, the simulated stress at the point of failure from the elastic region was used as an initial estimate. Additionally, several other simulations were performed in the vicinity of this yield stress to create a curve relating the characteristic failure load and the known yield stress. As a result, the yield/failure stress for NU-1000-bip was calculated to
be 2.45 ± 0.07 GPa, nearly an order of magnitude higher than the 298 ± 22 MPa of NU-1000-ben.

The load–displacement results from the simulations matched remarkably well with the experimentally measured load–displacement behavior for NU-1000-bip (Figure 2.13c). The simulations matched less well for NU-1000-ben, which was possibly due to the NU-901 phase impurities disrupting the structure.

Notably, the simulated load–displacement response for NU-1000-bip had a non-zero slope post-failure. This differed from what one might expect for an elastic–perfectly plastic material, but it can be explained by examining the stress distribution within the particle (Figure 2.15). The non-zero loading slope post-failure was a result of the particle geometry; even after some of the material had yielded, there was other material further from the center that continued to deform elastically, resulting in a non-zero loading slope after yield. (More detail can be found in our published paper.275)
Figure 2.15. (a) The shape of the stress distribution at the point of failure assuming elastic–perfectly plastic behavior. Colors correspond to stress contours for (b) NU-1000-bip and (c) NU-1000-ben. Stresses are von Mises stresses with units of TPa. Yield stresses are 2.5 GPa and 300 MPa for NU-1000-bip and NU-1000-ben, respectively. Three distinct zones can be seen in the particle: (1) red, corresponding to fully yielded material; (2) green, corresponding to material that is elastically strained; (3) blue, corresponding to material that has undergone minimal deformation.

2.4 Conclusion

The mechanical properties of phase-pure NU-1000, NU-901-containing NU-1000, and silica reinforced NU-1000 were investigated. As the NU-901 phase impurity in NU-1000 was removed by employing a different modulator, the particle morphology changed to a more uniform structure with a smoother surface, the effective elastic modulus increased from 3 GPa (NU-1000-ben) to 21 GPa (NU-1000-bip), and the yield/failure stress was increased from 300 MPa to 2.5 GPa. These results suggest that a uniform structure might be important for MOF materials to be more robust. Silica reinforcement in the mesopores of NU-1000 (SiO$_3$(OH)$_y$@NU-1000) was found to increase the load at failure from 2000
μN to 3000–4000 μN. This result implies a possible modification method to escalate the mechanical properties of MOFs. This method might also be applicable to other MOF materials to enhance their mechanical properties.
Chapter 3

Development of an Acid-Free Nanocasting Method for Metastable Ce-MOFs


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This work was done in collaboration with Dr. Camille Malonzo and Jiaxin Duan (nanocasting (Ce)UiO-66 and (Ce)UiO-67 and performing related characterization), and Wenyang Zhao (creating simulated XRD patterns using SKIP software).
3.1 Introduction

As discussed in Chapter 1, in the past two decades, the properties and applications of MOF materials have been extensively studied. They have been tested in the context of many crucial industrial applications, among which heterogeneous catalysis is a very important part.\textsuperscript{89-93} Being popular as heterogeneous catalysts, MOFs have several intrinsic merits, including high specific surface areas, tunable pore sizes, and abundant catalytically active sites. The catalytically active components in MOF materials are clusters, which are composed of several metal atoms or oxygen and metal atoms (usually within one nanometer). Many metal species have been synthesized into the MOF clusters, which endow MOFs the capabilities to be used in different reactions.\textsuperscript{101} Furukawa et al. summarized the structures of many commonly seen clusters,\textsuperscript{71} among which several classical ones are shown in Figure 3.1(a).
Figure 3.1. (a) Structures of several classical clusters in MOFs. Color code: Cu (orange),\textsuperscript{280} Cr or Fe in MIL-101 (green),\textsuperscript{281} Ce or Zr (creamy white), H (white),\textsuperscript{282-283} Ni (green) in DUT-9;\textsuperscript{284} O (red). (b) Graph showing the relationship between surface energy and size for the active component in catalysts. The increased surface energy with minimized sizes of the catalytically active components indicates the importance of keeping them separated during the synthesis. Graph (b) was adapted with permission from ref.\textsuperscript{10}, Copyright (2013), American Chemical Society.
The specific activity of a catalytic component in the catalysts usually goes up with diminished size because of the increased surface area and per-atom reactivity, while its surface energy also rises due to the increased surface free energy (Figure 3.1b). Nowadays, commercial catalysts are often synthesized via well-established methods such as co-precipitation, chemical decomposition, impregnation, physical or chemical vapor deposition.\textsuperscript{285} Their active components normally have sizes of tens or hundreds of nanometers, which correspond to “Nano-” in Figure 3.1b, while MOF catalysts can be categorized into “Subnano-”. Compared to catalysts prepared by traditional approaches, MOFs usually exhibit higher surface area, better-controlled size/spatial distribution of the active components. Compared to single-atom catalysts, MOFs have much higher loading of the active components (Table 3.1), so they theoretically have higher overall mass efficiency.
Table 3.1. Applications and loadings of active metals reported for a selection of single-atom catalysts.

<table>
<thead>
<tr>
<th>single-atom catalyst</th>
<th>application</th>
<th>loading*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co@N-GO\textsuperscript{286}</td>
<td>H\textsubscript{2} evolution reaction</td>
<td>0.57 at%</td>
</tr>
<tr>
<td>Fe@SiO\textsubscript{2}\textsuperscript{287}</td>
<td>CH\textsubscript{4} dehydrogenation</td>
<td>0.5 wt%</td>
</tr>
<tr>
<td>Pd@TiO\textsubscript{2}\textsuperscript{288}</td>
<td>benzaldehyde hydrogenation</td>
<td>1.5 wt%</td>
</tr>
<tr>
<td>Au@CeO\textsubscript{2}\textsuperscript{289}</td>
<td>CO oxidation</td>
<td>0.3 wt%</td>
</tr>
</tbody>
</table>

* The loadings of metal species in MOFs are usually not reported because they are abundant. If the MOF NU-1000 is taken for an example, the loading of zirconium is 25.1 wt%.

One hindrance for the development of MOFs as catalysts is their limited thermal stability because they contain organic components naturally. MOFs usually decompose at temperatures higher than 350 °C, resulting in aggregation of the clusters and loss of the porosity. To extend the application range of the catalytically active clusters in MOFs, our group previously reported silica nanocasting in the mesopores of NU-1000 MOF, in which the silica-Zr\textsubscript{6} cluster nanohybrid product (Zr\textsubscript{6}@SiO\textsubscript{2}) maintained the catalytically active Zr\textsubscript{6} clusters even after thermal treatment at 600 °C.\textsuperscript{135}

Inspired by this work, the silica nanocasting method was attempted on other MOF materials to achieve heterogeneous catalysts with different metal species. Several Ce-MOFs ((Ce)UiO-66, (Ce)UiO-67, and (Ce)MOF-808) were chosen as the study targets for two reasons: 1) In these Ce-MOFs, the Ce\textsubscript{6}O\textsubscript{8} clusters are in the shape of Ce\textsubscript{6} octahedron
with each face capped with $\mu_3$-O or $\mu_3$-OH groups, which is similar to that of the $\text{Zr}_6\text{O}_8$ clusters in NU-1000 (**Figure 3.1a**). The high symmetry of this type of clusters endows their MOF matrixes extra chemical and thermal stabilities, which might potentially lead to successful nanocasting. 2) Cerium oxide is a well-known catalyst and catalyst support due to its extraordinarily reversible oxygen storage capacity and strong metal-support interactions with many precious metal species. Cerium oxide has been widely applied as an active component in many industrial redox processes, such as exhaust conversions in automobiles (Pt (Rh)/CeO$_2$-Al$_2$O$_3$, Pt (Rh)/CeO$_2$-ZrO$_2$), hydrocarbon reforming (Pd/CeO$_2$, Cu/CeO$_2$, Ni/CeO$_2$), and water gas shift reaction (Pt (Pd, Rh)/CeO$_2$, CeO$_2$/Au, Au/CeO$_2$/TiO$_2$).

We demonstrate in this chapter an improved silica nanocasting method, which can be applied to metastable Ce-MOFs. In the new nanocasting method, previously used HCl(g) catalyst was avoided, and the TMOS was hydrolyzed and condensed only in the presence of water. The investigated Ce-MOFs are (Ce)UiO-66, (Ce)UiO-67, and (Ce)MOF-808 (**Figure 3.2**). Nanocast (Ce)MOF-808 was found to support and separate the clusters the best. The development of this new nanocasting route and methods for the characterization of Ce$_6$ clusters are discussed. Additionally, the redox activity of the nanocast (Ce)MOF-808 is investigated.
3.2 Experimental

3.2.1 Materials

The following chemicals were used as received: \((\text{NH}_4)_2\text{Ce(NO}_3)_6\) (≥98.5%), benzene-1,4-dicarboxylic acid (H\(_2\)bdc, 98%), benzene-1,3,5-tricarboxylic acid (trimesic acid, H\(_3\)btc, 95%), tetramethyl orthosilicate (TMOS, 98%), and methanol (≥ 99.8%) from Sigma-Aldrich; biphenyl4,4’-dicarboxylic acid (H\(_2\)bpdc, (≥97.0%) from TCI America; hydrochloric acid (36.5–38.0%) from BDH Chemicals; N,N-dimethylformamide (DMF, 99.8%) from Macron Fine Chemicals; dimethylsulfoxide (DMSO, 99.9%) from Fisher Chemical. Deionized water produced on-site with a minimum resistivity of 18.2 MΩ·cm was used in all experiments.

3.2.2 Synthesis of MOF Materials

\((\text{Ce})\text{UiO-66 and (Ce)UiO-67.}\) The procedure for the preparation of \((\text{Ce})\text{UiO-66 and (Ce)UiO-67 was adapted from a previous publication.}\) To synthesize \((\text{Ce})\text{UiO-66, H}_2\text{bdc (35.4 mg, 0.213 mmol) was dissolved in DMF (1.2 mL). In a separate vial, (NH}_4)_2\text{Ce(NO}_3)_6 \)
(117 mg, 0.21 mmol) was dissolved in deionized water (0.4 mL). The two solutions were mixed and heated at 100 °C for 15 min. The product, (Ce)UiO-66, was washed twice with DMF and then twice with methanol prior to air-drying. The MOF was finally activated at 130 °C for 12 h. (Ce)UiO-67 was prepared similarly, with the following exceptions: H₂bpdc (51.6 mg, 0.213 mmol) was used as the linker, the reaction time at 100 °C was increased from 15 min to 20 min, and the sample was washed twice with DMSO instead of DMF.

(Ce)MOF-808. The procedure for the preparation of (Ce)MOF-808 was adapted from a previous publication.⁹⁵ To synthesize (Ce)MOF-808, H₃btc (22.4 mg, 0.106 mmol) was introduced into a vial containing a mixture of DMF (1.2 mL) and formic acid (0.578 mL, 6.83 mmol). A solution of (NH₄)₂Ce(NO₃)₆ (0.6 mL, 0.533 M) was then added to this mixture. The vial was heated at 100 °C for 15 min. The product, (Ce)MOF-808, was washed twice with DMF and then four times with acetone prior to 70 °C air-drying. The MOF was finally activated at 100 °C for 12 h.

3.2.3 Silica Nanocasting

Silica nanocasting with acid catalyst. A casting solution composed of 300 μL of TMOS, 5 μL of methanol and 5 μL H₂O was first mixed in a vial. It was then added to 30 mg of the MOF and allowed to infiltrate the MOF particles for 24 h. Afterwards, the sample was washed with methanol to remove any TMOS from the external surface of the particles, and heated at 40 °C for 5 min to dry. To induce hydrolysis and condensation of the TMOS in the sample, the sample was first exposed to HCl(g) for 24 h at room temperature. This
was followed by heat treatment in a closed vial at 60 °C for another 24 h. Finally, the sample was calcined at 500 °C for 1 h in static air to remove the organic linkers from the structure. A temperature ramp rate of 2 °C min⁻¹ was used for calcination.

*Silica nanocasting without acid catalyst.* A casting solution composed of 300 µL of TMOS, 75 µL of methanol and 50 µL H₂O was first mixed in a vial. It was then added to 30 mg of the MOF and allowed to infiltrate the MOF particles for 24 h. The casting solution was removed by centrifugation and decantation. Afterwards, the sample was washed with methanol to remove any TMOS from the external surface of the particles, and heated at 40 °C for 5 min to dry. To induce hydrolysis and condensation of the TMOS in the sample, the sample was heated in a closed vial at 80 °C for 24 h. Finally, the sample was calcined at 500 °C for 1 h to remove the organic linkers from the structure. A temperature ramp rate of 2 °C min⁻¹ was used for calcination.

### 3.2.4 Characterization

Fourier-transform infrared spectroscopy (FT-IR) data were collected using a Nicolet Magna-IR 760 spectrometer. Ground samples were placed between two KBr windows for FT-IR measurements. Scanning electron microscopy (SEM) measurements were performed using a JEOL 6700 scanning electron microscope operated using a 5.0 kV accelerating voltage. Prior to SEM analysis, all samples were sputter coated with a conductive thin film (70 Å) of Pt. X-ray diffraction (XRD) patterns were collected using an X’Pert Pro diffractometer with an X’Celerator detector. A Co anode (Kα, λ = 1.789 Å) operating at 45 kV and 40 µA was used as the radiation source. N₂ sorption analyses were
conducted using a Quantachrome Autosorb iQ2. The MOF samples were degassed prior to the analysis at 1 mTorr for 12 h at 130 °C. Scanning electron microscopy-energy-dispersive X-ray spectroscopy (EDS) compositional analyses were acquired using a JEOL JXA-8900 electron microprobe operated at 15.0 kV accelerating potential. Samples were coated with a thin film (70 Å) of carbon prior to SEM-EDS measurements. Scanning transmission electron microscopy (TEM) was performed using an FEI Tecnai G2 field-emission S/TEM operating at an accelerating voltage of 120 kV. The nanocast samples were loaded onto TEM grids from ethanol suspensions. X-ray photoelectron spectroscopy (XPS) was performed using a VersaProbe III instrument, with an Al Kα X-ray source.

3.3. Results and Discussion

3.3.1. Development of Acid-Free Nanocasting Method for Ce-MOFs

In our previous work on nanocasting NU-1000, a TMOS/MeOH/H₂O mixture was applied as the casting liquid. HCl(g) was then used as an acid catalyst to facilitate the hydrolysis and condensation of TMOS inside the pores of NU-1000. Silica formed as the new support while the original organic framework decomposed during the following calcination. However, Ce₆ clusters aggregated and formed CeO₂ nanoparticles while the same method was applied on Ce-MOFs (Figure 3.3). The different behaviors of Ce-MOFs and NU-1000 during the silica nanocasting process were conjectured to be due to their different stabilities toward HCl(g). The Ce-MOF structures might be unstable compared to NU-1000 and was destroyed during the HCl(g) treatment, which led to the agglomeration of Ce₆ clusters.
Figure 3.3. XRD patterns of (a) nanocast Ce-MOFs prepared by nanocasting utilizing HCl\(_{(g)}\) catalyst. Average grain sizes estimated from line broadening using the Scherrer equation are \(\approx 5\) nm CeO\(_2\) for nanocast (Ce)MOF-808, \(\approx 7\) nm CeO\(_2\) for nanocast (Ce)UiO-67, and \(\approx 17\) nm CeO\(_2\) for nanocast (Ce)UiO-66; (b) nanocast NU-1000 utilizing HCl\(_{(g)}\) catalyst (which is named as Zr\(_6\)@SiO\(_2\)) after calcination at 500, 600, or 700 °C. The XRD pattern of NU-1000 calcined at 500 °C in air is also shown for comparison. Figure b was reproduced with permission from ref.\(^{135}\), Copyright (2016), American Chemical Society.

To study the roles of H\(^+\) and Cl\(^-\) in the decomposition of Ce-MOFs, their stabilities were tested by exposing them to HCl\(_{(g)}\) vaper, immersing them in NaCl, and HNO\(_3\) solutions for 24 h, respectively (Figure 3.4). After being immersed in NaCl solution, the major peaks of three MOFs were still observed, indicating their stability in NaCl solutions. Notably, the XRD peaks of (Ce)UiO-66 became wider, suggesting this material is the least stable MOF among those three. After being immersed in HNO\(_3\), both (Ce)UiO-66 and (Ce)UiO-67 lost the characteristic MOF peaks but (Ce)MOF-808 still maintained the most intense peaks between 8 and 10° 2θ. After the exposure to HCl\(_{(g)}\), all three MOFs lost their characteristic
peaks, indicating the decomposition of the ordered MOF structures. This result suggests that ligand protonation plays a major role in the destabilization of Ce-MOFs.
Figure 3.4. XRD patterns of (Ce)UiO-66, (Ce)UiO-67, and (Ce)MOF-808 after being immersed in 3 mol/L NaCl, and 3mol/L HNO₃ solutions, and exposed to HCl(g) for 24 h. The samples were then washed with acetone and dried at 70 °C for 10 min.
To overcome the drawback of using an acid catalyst, a new acid-free nanocasting method was developed. The general strategy was to induce the hydrolysis and condensation of TMOS in the presence of H₂O only. In this method, the casting fluid was still a mixture of TMOS/MeOH/H₂O, but the percentages of MeOH and H₂O were increased. Additionally, because of the lack of the HCl acid catalyst, the reaction temperature for the hydrolysis and condensation of TMOS was increased from 60 to 80 °C. With the decreased percentage of TMOS in the casting fluid, the amount of introduced silica would be less, but the overall reaction environment became milder. The same calcination conditions were maintained as for the acid-catalyzed process (500 °C in air). It was observed that via using the acid-free nanocasting method, the peaks corresponding to CeO₂ became broader in Figure 3.5a compared to the ones in Figure 3.3a, indicating the presence of smaller CeO₂ species. Therefore, the acid-free nanocasting method was proved to be successful in mitigating the aggregation of the Ce₆ clusters.

### 3.3.2 Investigation of the Size of CeO₂ in the Nanocast Ce-MOFs

The Scherrer equation has been widely applied for the estimation of crystallite size in XRD technique (equation 1),

\[ D_{hkl} = \frac{k\lambda}{B_{hkl}\cos\theta} \]  

in which \( D_{hkl} \) is the crystalline size of the material in the direction perpendicular to the (hkl) planes, \( k \) is the crystallite-shape factor, \( \lambda \) is the wavelength of the incident X-ray, and \( B_{hkl} \) is the full-width at half-maximum (FWHM) of the peak at a certain \( \theta \) diffraction angle.
Generally speaking, the wider the XRD peak is, the smaller the crystallite size is. Although there is no clear lower size limit for the application of Scherrer equation, there is a concentration limit for a component to exhibit good enough peak profile. When a material contains ultrasmall species, the majority must be the supporting matrix so that the small species do not aggregate. In this case, the XRD pattern will be mainly from the matrix species, resulting in a low peak intensity for the interesting small species. Additionally, a small crystalline size \( D_{hkl} \) means a large \( B_{hkl} \) value for the peak, which increases the difficulty of fitting the peak. For example, the FWHM value of (111) peak for a 2 nm ceria particle is 5.7°, and it is 11.5° for a 1 nm ceria particle (according to the ceria reference pattern in Figure 3.5a). Fitting such broad peaks with relatively low intensity is very challenging. In the current study, SKIP software was used instead for the estimation of crystallite size for CeO\(_2\) in the nanocast product. Via SKIP, one can generate XRD patterns simulated from certain amount of CeO\(_2\) unit cells stacked together. By comparing the shape of the nanocast Ce-MOFs peaks to the simulated CeO\(_2\) peaks, the estimated grain size for acid-free nanocast (Ce)UiO-66 and (Ce)UiO-67 was around 2 nm, and that for acid-free nanocast (Ce)MOF-808 was under 1 nm.
The size of the ceria in the nanocast Ce-MOF materials was further investigated by TEM (Figure 3.6) and Raman spectroscopy (Figure 3.7). Based on the TEM images, nanocast (Ce)UiO-66 and (Ce)UiO-67 both showed CeO$_2$ particles with sizes around 2 nm whereas nanocast (Ce)MOF-808 did not show any CeO$_2$ particles. Raman spectroscopy is a useful tool for detecting short-range order. A characteristic Raman peak at 461 cm$^{-1}$ from the CeO$_8$ vibration ($F_{2g}$) has been reported for CeO$_2$ materials.$^{303}$ Nanocast (Ce)UiO-66 showed the $F_{2g}$ peak, whereas the nanocast (Ce)MOF-808 did not. However, when a laser beam was applied to sinter the nanocast (Ce)MOF-808 material, the $F_{2g}$ peak appeared.
This implies that the Ce species in the nanocast (Ce)MOF-808 were likely maintained as the Ce$_6$O$_8$ clusters, the same as those in the original (Ce)MOF-808.

**Figure 3.6.** TEM images of (a) nanocast (Ce)UiO-66, (b) nanocast (Ce)UiO-67, and (c) nanocast (Ce)MOF-808.
Figure 3.7. Raman spectra of nanocast (Ce)UiO-66, nanocast (Ce)MOF-808, and sintered nanocast (Ce)MOF-808. The peak at 461 cm\(^{-1}\) corresponding to a CeO\(_8\) vibration appears when multiple CeO\(_2\) unit cells are stacked. However, a single Ce\(_6\)O\(_8\) cluster does not show this peak due to the lack of the CeO\(_8\) environment. Color code: Ce (red), O (white).

From the XRD, TEM, and Raman results, it was concluded that the silica support was more effective at preventing cluster agglomeration in nanocast (Ce)MOF-800 than in the other two MOFs. This was possibly due to its lower linker connectivity (6) compared to (Ce)UiO-66 and (Ce)UiO-67 (12), which results in a larger window size. This feature makes its structure more open and pores more accessible to the TMOS precursor. This conclusion was further supported by the SEM-EDS results, from which the Si/Ce\(_6\) ratio of each nanocast product was determined to be 8.13 (nanocast (Ce)UiO-66), 9.99 (nanocast
(Ce)UiO-67), and 10.41 (nanocast (Ce)MOF-808), respectively. The SEM-EDS result indicated that most silica was introduced into the (Ce)MOF-808 during the infiltration of TMOS precursor. Notably, the weight percentage of cerium in the nanocast (Ce)MOF-808 was 51 wt%, far exceeding the reported values for single-atom catalysts in Table 3.1. This result implies that the nanocasting method is a useful tool to achieve heterogeneous catalyst with abundant loading of active metal oxide with sizes less than 1 nm. Since the nanocast (Ce)MOF-808 material had the most well-dispersed CeO₂ grains, the following studies were conducted mainly on this material.

3.3.3 Presence of SiO₂ Inside the Pores of (Ce)MOF-808

From the previous discussion, it was shown that in the nanocast (Ce)MOF-808 material, silica supported the Ce₆ clusters and maintained them separated. However, it was not elucidated whether the silica was actually introduced into the pores of (Ce)MOF-808 or stayed outside. The incorporation of silica into the pores of (Ce)MOF-808 was confirmed by IR and N₂ isotherm (Figure 3.8). In the IR spectra, for the infiltrated (Ce)MOF-808 (refers to the (Ce)MOF-808 sample after the introduction, hydrolysis, and condensation of the TMOS precursor), a new peak at around 1100 cm⁻¹ was observed compared to (Ce)MOF-808, which corresponds to the Si-O-Si stretching vibration.¹³⁵, ³⁰⁴ This peak was maintained in the final nanocast (Ce)MOF-808 product, indicating the presence of silica in both samples. It was also observed that the peak corresponding to the asymmetrical vibration of COO⁻ appeared in both (Ce)MOF-808 and infiltrated (Ce)MOF-808 but not in the nanocast (Ce)MOF-808. This indicated that the MOF structure was
maintained during the infiltration, hydrolysis and condensation of the TMOS precursor but destroyed after the calcination. The N\textsubscript{2} isotherm showed that the surface area and pore volume of the (Ce)MOF-808 both decreased after the introduction of silica. Additionally, the pore size of (Ce)MOF-808 shifted from ~2.2 nm to ~1.5 nm, which was due to partial pore filling with silica.
**Figure 3.8.** (a) FT-IR spectra of (Ce)MOF-808, infiltrated (Ce)MOF-808, nanocast (Ce)MOF-808, and SiO$_2$ gel as the reference. Infiltrated (Ce)MOF-808 refers to the (Ce)MOF-808 with silica formed inside from the hydrolysis and condensation of the TMOS precursor; (b) N$_2$ isotherm of (Ce)MOF-808 and infiltrated (Ce)MOF-808. The inset figure is the pore size distribution of (Ce)MOF-808 and infiltrated (Ce)MOF-808 calculated from density functional theory. Pore size distributions were calculated by NLDFT using a slit pore model.

### 3.3.4 Redox Activity of Nanocast (Ce)MOF-808

Considering the redox activity of cerium species, it is interesting to investigate their redox properties in the developed nanohybrid. XPS was applied for this study. Ce(IV) and Ce(III) have some overlapping characteristic peaks in the XPS spectra, which makes it difficult to deconvolute and calculate accurate Ce(IV)/Ce(III) ratios. However, Ce(IV) has unique peaks at 917, 907, and 889 eV.$^{305}$ Based on this knowledge, the majority of the
cerium species in nanocast (Ce)MOF-808 was determined to have oxidation number IV (Figure 3.9a). After being exposed to a flow of 95% N₂ and 5% H₂ at 750 °C for 1 h, the cerium species turned to Ce(III), which was indicated by the disappearance of the peak at 917 eV. They were reoxidized to Ce(IV) after being heated at 750 °C for 1 h under air. Notably, the peaks at 907 and 889 eV were more pronounced in the reoxidized sample compared to the original nanocast (Ce)MOF-808, indicating that some Ce(III) was also present in the original nanocast (Ce)MOF-808. Additionally, it was concluded on the basis of XRD patterns (Figure 3.9b) that during this redox cycle no aggregated CeO₂ formed. This indicated that the Ce species in the nanocast (Ce)MOF-808 could switch oxidation states while the silica prevented cluster aggregation.
Figure 3.9. (a) XPS spectra of nanocast (Ce)MOF-808 undergoing a redox cycle. The reduction conditions are 750 °C for 1 h under a flow of 95% N₂ and 5% H₂, and the deoxidation conditions are 750 °C for 1 h in air. (b) XRD patterns of nanocast (Ce)MOF-808, reduced nanocast (Ce)MOF-808, and reoxidized nanocast (Ce)MOF-808.

3.4 Conclusion

In this chapter, a new silica nanocasting method was developed with no acidic catalyst present. The acid-free nanocasting method mitigated the aggregation of Ce₆ clusters in the nanocast Ce-MOF materials compared to the original nanocasting method. Among the three tested Ce-MOFs ((Ce)UiO-66, (Ce)UiO-67, (Ce)MOF-808), (Ce)MOF-808 was found to have the least disturbed Ce₆ clusters after nanocasting. In fact, Raman spectra suggested that the original cluster structure in (Ce)MOF-808 was maintained after nanocasting. This was possibly due to its larger pore window sizes compared to the other
two, which resulted in a more efficient silica infiltration. The weight percentage of cerium in the developed nanohybrid product was 51 wt%, much higher than in typical single-atom catalysts. Additionally, the Ce species in the nanohybrid material can switch oxidation states between IV and III at 750 °C without aggregation. The development of this new type of acid-free nanocasting method provides opportunities for synthesizing more nanohybrid materials containing various types of metal oxo clusters.
Chapter 4

Development of Methods for Carbon Nanocasting in NU-1000


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This work was done in collaboration with Dr. Karena W. Chapman and Dr. Ana E. Platero-Prats (performing synchrotron X-ray diffraction experiments and related data analysis) of Argonne National Laboratory, Dr. Matthias Thommes and Dr. Francisco Sotomayor (performing high-resolution argon isotherm measurements and related data analysis) of Quantachrome Instruments, Prof. R. Lee Penn and Dr. Thomas E. Webber (collecting TEM images), Prof. Joseph T. Hupp, Prof. Omar K. Farha, and Timothy C. Wang (synthesizing NU-1000) of Northwestern University. Prof. Paul J. Dauenhauer, Dr. Omar A. Abdelrahman, and Ms. Kristeen E. Joseph contributed to this work by performing TPD measurements and related data analysis.
4.1 Introduction

In the previous chapter, silica nanocasting in MOFs was discussed, through which inorganic nanocomposites could be achieved with high loadings of nanosized metal oxide clusters that were separated and supported by silica.\textsuperscript{135,141} The resulting silica framework acted as an inert scaffold to stabilize the clusters and provide the desired porosity at rather high temperatures. In silica nanocasting, most focus was put on preserving the catalytically active clusters, whereas the organic linkers were regarded valueless and removed during the calcination process. Considering these systems from a different perspective, one can find that the organic linkers are ideal sources to prepare pure or doped carbon materials. Indeed, much research has been performed with the goal to develop carbon-based nanomaterials using MOFs as precursors, through which the application scope of MOF related materials can be extended to electrocatalysis and energy storage.\textsuperscript{80,306}

The major technique of fabricating carbon-based nanomaterials from MOFs is pyrolysis under N\textsubscript{2} or Ar, during which the organic linkers are converted into carbon. Depending on the purpose of the study, the metal or metal oxo species can either be removed to form porous carbon (or non-metal doped carbon) or retained to form carbon–metal or metal oxide nanohybrids.\textsuperscript{80} Using MOFs as precursors to prepare carbon-based nanomaterials has several advantages, including that (1) the structural and compositional varieties of MOF precursors can lead to the formation of desired architectures (such as nanocubes, nanowires, and nanosheets) containing specific metal species;\textsuperscript{307-311} (2) periodicity of the metal species and pore structures in original MOFs could be retained to some degree after pyrolysis. To date, MOFs have been applied to synthesize various types
of carbon-based nanomaterials, of which the synthesis and application will be discussed as follows.

*Using MOFs to create porous carbon nanomaterials.* For this purpose, metal or metal oxo species in MOFs are removed via certain methods after pyrolysis, leaving only porous carbon as the products. Common approaches to remove metals or metal oxo groups include high-temperature vaporization, which works well for Zn-, Al-, and Mg-MOFs, and acid etching, which works well for Co- and Al-MOFs.\(^{80, 152, 312-313}\) As mentioned before, the structures of the derived carbon nanomaterials can be tuned via choosing specific MOF precursors and appropriate synthetic techniques. For example, Xia et al. reported that carbon nanotubes could be achieved through pyrolyzing ZIF-67 in Ar/H\(_2\), during which the Co species catalyzed the growth of the nanotubes.\(^{307}\) The Co was then removed through acid etching. Pachfule et al. synthesized carbon nanorods by pyrolyzing MOFs, and they discovered that the nanorods could be further exfoliated to form graphene nanoribbons through sonication in KOH solution and thermal activation.\(^{308}\) In addition to pure carbon nanomaterials, non-metal doped carbon nanomaterials (such as with nitrogen, boron, sulfur, and phosphorus) could also be synthesized through similar processes.\(^{151}\) The incorporation of these elements is often achieved through pyrolyzing MOFs containing functionalized organic linkers. For example, zeolitic imidazolate frameworks are always used to introduce N atoms.\(^{314-316}\)

MOF-derived carbon and doped-carbon nanomaterials exhibit high surface areas with tunable pore textures and high electrical conductivity.\(^{316}\) These merits make them good candidates in various applications, such as gas/liquid storage, contamination removal,
supercapacitor, fuel cells, and electrocatalysis. For example, Yang et al. demonstrated in 2012 that the porous carbon derived from MOF-5 exhibited the highest H₂ storage capacity among all the reported materials due to its high surface area and ultramicroporosity. Torad et al. reported the fabrication of a porous carbon material from ZIF-67 as an electrode in electric double-layer capacitors. The material showcased a rather high specific capacitance of 238 F g⁻¹.

Using MOFs to create carbon–metal or metal oxide (C–M(MO)) nanohybrids. When the metal or metal oxo species are retained during the synthetic procedure, the resulting products are C–M(MO) nanohybrids. C–M(MO) nanohybrids have been tested widely in various electrocatalytic processes, such as oxygen reduction reaction (ORR), oxygen evolution reaction (OER), CO₂ reduction reaction, and H₂ evolution reaction (HER). The review written by Zhang et al. has a comprehensive summary of the reported carbon–metal nanohybrids and their performances in certain reactions. Additionally, the C–MO nanohybrid has been applied as anode material for lithium ion batteries. Depending on the metal or metal oxide components in the products, C–M(MO) nanohybrids can be further divided into two subcategories: (1) direct pyrolysis of MOFs usually results in the aggregation of clusters, and the products have metal or metal oxide nanoparticles (NPs). Notably, the formation of metal oxide nanoparticles requires an extra oxidation step after pyrolysis in some cases. (2) through specific designs on the MOF structures and synthetic methods, the products from pyrolysis can contain single-atom metal species.
The pursuit of single-atom metal species in carbon–metal nanohybrids was motivated by the idea that a single-atom catalyst had extremely high surface area and per-atom reactivity, so it could exhibit extraordinary performance in the catalytic processes. However, delicate experimental designs are usually required to ensure the achievement of single atoms during heat treatment. For example, Yin et al. achieved a carbon–Co single atom nanohybrid through pyrolyzing a carefully designed ZIF-67 MOF. They applied a mixture of Zn and Co salts as the precursor to synthesize a Zn/Co-ZIF-67 MOF (some of the clusters are Zn clusters and the others are Co clusters), in which the Zn played the role of diluting the Co concentration. After pyrolysis and removal of Zn at a high temperature, the product had a 4 wt% loading of the Co single atoms in the nanohybrid. Notably, similar to other single-atom catalysts discussed in Chapter 1, the carbon–metal single atom nanohybrids reported so far often showed high turn-over frequency (TOF) towards certain electrocatalytical reactions, but suffered from low overall-mass efficiency due to the limited loadings of single atoms.

Compared to single atoms, nanoparticles are easier to achieve in carbon–metal nanohybrids with relatively high loadings. Moreover, if other metal precursors are introduced into the MOFs or the MOFs are synthesized to contain various types of metal species in the first place, the pyrolyzed products become carbon–metal alloy NP nanohybrids, which can exhibit superior performance in electrocatalysis due to the synergistic effects from certain combinations of metal species. For example, Su et al. reported the fabrication of a carbon–Ru/Co alloy nanohybrid. The alloy exhibited higher catalytical activity in HER compared to Co nanoparticles by themselves. Density function
theory calculations indicated that the available number of electrons for transfer in the alloy is larger than that in Co nanoparticle, leading to the higher HER activity. Additionally, in some C–M(MO) nanoparticle nanohybrids, the nanoparticles, such as cobalt or cobalt oxide NPs and carbon have shown strong synergistic effects, which resulted in superior activity in ORR/OER. This type of effect has not been observed in carbon–metal single atom nanohybrids. Despite these advantages, the drawback of carbon–metal or metal oxide NP nanohybrids is the wide size-distribution of the embedded NPs.

Here, we demonstrate the synthesis of a carbon–oxometal cluster nanohybrids through a carbon nanocasting method. In this method, NU-1000 MOF was applied as the precursor, and furfuryl alcohol was introduced into the pores of NU-1000 through vapor transfer. Via pyrolysis under N₂, a carbon–oxozirconium cluster nanohybrid (Zr₆@C, Zr₆ refers to the Zr₆O₈ clusters) was achieved. Due to the extra carbon support from the furfuryl alcohol precursor, the abundant Zr₆ clusters of original NU-1000 were retained and separated in the product.

Preserving the Zr₆ clusters in the product provides the opportunity to introduce other functionalities through modifying these Zr₆ clusters. For example, Zr₆ clusters have been reported as good anchor sites for other species, such as Ni atoms, Ir atoms, Cu₂O clusters, and Pt₄ clusters. These implanted species can possibly be retained together with the Zr₆ clusters through pyrolysis, resulting in the formation of new types of C–M(MO) nanohybrids with plentiful uniform-sized catalytically active sites.

In this chapter, the development of this carbon nanocasting approach is discussed. The structure and properties of the Zr₆@C nanohybrids, including their composition,
morphology, pore structure, and accessibility of the clusters are investigated using multiple 
characterization methods. To evaluate the potential application of the nanohybrid material 
as an electrocatalyst, its conductivity is also studied.

4.2 Experimental

4.2.1 Materials

Chemicals used in this study were obtained from the following sources: ethanol 
(anhydrous, 200 proof) from Pharmco-AAPER; \textit{N,N}-dimethylformamide (DMF, certified 
ACS, 99.9%), acetone (certified ACS, 99.7%) from Fisher Chemical; furfuryl alcohol 
(98%), methanol (>99.8%), hydrochloric acid (ACS reagent, 37%), benzoic acid (ACS 
reagent, 99.5%), and pyridine (99.8%) from Sigma-Aldrich; \textit{1,3,6,8}-tetrakis\textit{(p-benzoic 
acid)pyrene} (H$_4$TBAPy) was synthesized following a previously reported procedure.$^{268}$

Deionized water was purified to a minimum resistivity of 18.2 M\textgreek{O}·cm with a Milli-Q 
PLUS reagent-grade water system and was used in all experiments.

4.2.2 Procedures of Carbon Nanocasting in NU-1000

NU-1000 was synthesized following a previously published method.$^{268}$ A mass of 30 
mg of NU-1000 was placed in an uncapped vial and the vial was put into an autoclave 
containing 10 mL of furfuryl alcohol (FA), taking care to prevent direct contact between 
the liquid FA and the NU-1000 powder. The autoclave was heated to 90 °C to create FA 
vapor. Different heating times (12 h, 24 h, 48 h, 72 h and 144 h) were examined for the 
infiltration step because the exposure time to the FA vapor affected the amount of FA
loaded inside the pores of NU-1000. The NU-1000 product loaded with FA is denoted as FA@NU-1000. Polymerization of FA inside the pores of NU-1000 was performed in a tube furnace at 250 °C for 6 h using a 5 °C/min temperature ramp rate and an N₂ flow of 1000 mL/min. NU-1000 with polymerized poly(furfuryl alcohol) inside the pores is denoted as PFA@NU-1000-xh (x represents the different infiltration times in hours). Pyrolysis of PFA@NU-1000 was performed in a tube furnace at 600 °C for 1 h using a 5 °C/min temperature ramp rate and an N₂ flow of 1000 mL/min. The product formed from pyrolysis is denoted as Zr₆@C-xh, where Zr₆ refers to [Zr₆(µ₃-OH)₄(OH)₄(OH₂)₄]⁸⁺ oxozirconium clusters (Figure 2.1).

4.2.3 Pyridine Adsorption

Pyridine was used as a probe molecule to test the presence and accessibility of Lewis and Brønsted acid sites. The Zr₆@C samples were first activated at 200 °C for 1 h under dynamic vacuum (< 200 mTorr) to remove any residual surface-adsorbed water. Then the samples were cooled down to room temperature and excess pyridine was added to soak the samples for 1 h under static vacuum. The samples were heated again at 200 °C for 1 h under dynamic vacuum (< 200 mTorr) to remove physisorbed pyridine and then cooled down to room temperature. Finally, the samples were analyzed by FT-IR spectroscopy. Alternatively, to increase the accessibility of the oxozirconium clusters, Zr₆@C was heated in static air at 300 °C for 30 min with a ramp rate of 14 °C/min prior to the pyridine adsorption experiment.
4.2.4 Ammonia Temperature-Programmed Desorption

Ammonia temperature-programmed desorption (TPD) experiments were performed in an automated chemisorption analyzer (Quantachrome Pulsar). In a typical ammonia TPD experiment, samples (~50 mg) were placed in a u-shaped quartz cell heated in a 65 mL min\(^{-1}\) flow of He (Minneapolis Oxygen, 99.999\%) to 873 K at a ramp rate of 20 K min\(^{-1}\). Subsequently, the sample was cooled to 333 K and held there for 30 min. The flow was then switched to ammonia (Minneapolis Oxygen, anhydrous) at 35 mL min\(^{-1}\) for 10 min, allowing the ammonia stream to saturate the sample, followed by a purge in He for 30 min to remove excess ammonia. The sample was then heated to 373 K at a fixed linear ramp rate of 20 K min\(^{-1}\) under a stream of He and held there for 30 min to remove any weakly adsorbed ammonia. The TPD was then performed by heating to 873 K at a fixed linear ramp rate of 10 K min\(^{-1}\) under a stream of He, where all effluent from the sample was passed through a thermal conductivity detector. To better ascertain the identity of peaks in the ammonia TPD profile, H-BEA (Zeolyst, CP814E) and Na-Y (Zeolyst, CBV 100) were tested as reference samples for Brønsted and Lewis acidity, respectively. Prior to their analysis with ammonia TPD, both reference samples were calcined in a stream of air (Minneapolis Oxygen, Ultra Zero Grade) at 823 K for 12 h with a ramp rate of 1 K min\(^{-1}\). This part of experiment was performed by Omar A. Abdelrahman from the Dauenhauer group, Department of Chemical Engineering and Materials Science, UMN.
4.2.5 Characterization

FT-IR spectra were obtained in transmission mode using a Nicolet Magna 760 IR spectrometer, using powdered samples compressed between a pair of NaCl windows. Raman spectroscopy was performed using a WITec Alpha300R confocal Raman microscope with 514.5 nm laser radiation, and the scattering was detected using a DV401 CCD thermoelectrically-cooled detector. Powder X-ray diffraction patterns were collected using a PANalytical X’Pert Pro diffractometer. The X-rays were generated with a Co anode (Kα radiation, λ = 1.789 Å) operating at 45 kV accelerating voltage, 40 mA emission current. Scanning electron microscopy (SEM) was performed using a JEOL-6700 field emission scanning electron microscope with an accelerating voltage of 5.0 kV. All samples were coated with a 50 Å platinum film prior to SEM imaging or a 70 Å carbon film for EDS analyses. Gas sorption experiments were performed using ultra-high purity grade argon or nitrogen adsorptive. All samples were degassed under dynamic vacuum (0.003 mTorr) at 120 °C for 12 h before analyses. Nitrogen sorption experiments were performed on a Quantachrome Autosorb-iQ2 analyzer. Brunauer-Emmett-Teller (BET) surface areas were evaluated from the adsorption isotherms in the relative pressure range 0.01–0.20. High-resolution argon isotherm measurements were collected using an Autosorb-iQ2 MP analyzer (Quantachrome Instruments) over a relative pressure range of 10⁻⁷ to 1. The temperature was controlled using either a liquid argon cryogen bath or a Cryosync (Quantachrome Instruments). Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409 instrument. Samples were heated in air or nitrogen at a ramp rate of 5 °C/min. CHN elemental analysis was carried out at Atlantic Microlab (Norcross, GA).
Transmission electron microscopy (TEM) measurements were obtained using a FEI Tecnai T12 transmission electron microscope with an accelerating voltage of 120 kV and a LaB$_6$ filament. Samples were sonicated for 5 min in ethanol and then deposited onto carbon film-coated copper grids. Microtomed samples for TEM were prepared by embedding them in the epoxy resin Polybed 812 and heating at 60 °C overnight. The 65 nm sections were cut by using a Leica UC6 microtome and a Diatome diamond knife. Electrochemical impedance spectroscopy measurements were carried out with a Solartron S1 1287 electrochemical interface and a Solartron 1255B frequency response analyzer. The materials were ground to a powder and pressed into pellets using a hydraulic press at a ram pressure of 10 tons for 5 min. Each pellet contained around 100 mg of sample. The diameter and thickness of the pellet were measured with a vernier caliper.

4.2.6 Synchrotron X-ray Structural Analysis

Powder X-ray diffraction (XRD) data and total scattering data suitable for pair distribution function (PDF) analysis were collected at beamlines 17-BM and 11-ID-B, respectively, at the Advanced Photon Source at Argonne National Laboratory using 27.4 keV (0.45220 Å) and 58.6 keV (0.2114 Å) X-rays, respectively. Data were collected using an amorphous silicon-based area detector. Geometric corrections and reduction to one-dimensional data were carried out using GSAS-II. Lattice parameters and peak intensities were extracted from diffraction patterns via Le Bail whole-pattern fitting based on the reported structural model for NU-1000 (csq topology, $P6/mmm$, $a \sim 40$ Å, $c \sim 17$ Å). Lattice and pseudo-Voigt profile parameters were refined over a 0.5–10° 2θ range. Structure
envelopes were generated using the intensities of low-index reflections. Difference electron density (DED) maps were then obtained via subtraction of the envelope for pristine NU-1000 from the envelope for infiltrated NU-1000 samples. PDFs were obtained from the data within pdfgetX3 to a $Q_{\text{max}} = 24$ Å$^{-1}$. Differential PDFs were calculated by subtracting the PDF measured for the casting phase from the nanocast samples within Fityk. PDFs for structural models were simulated in PDFgui. The synchrotron X-ray diffraction data were collected by Ana E. Platero-Prats and Karena W. Chapman from Argonne National Laboratory.

4.3 Results and Discussion

4.3.1 Structural Characterization of PFA@NU-1000

Furfuryl alcohol (FA) was used as the carbon precursor for nanocasting, because its relatively small dimensions (0.84 Å × 0.64 Å × 0.43 Å) allow it to penetrate a wide variety of nanoporous templates.$^{152, 313, 320, 338-339}$ For infiltrating NU-1000, a vapor treatment was applied to introduce FA into its porous structure. FA vaporizes at 90 °C and gradually diffuses into the pores of NU-1000 to form FA@NU-1000. To polymerize the FA inside the pores of NU-1000, FA@NU-1000 was heated at 250 °C for 6 h to form PFA@NU-1000. The PFA@NU-1000 was then pyrolyzed at 600 °C for 1 h under N$_2$ to form Zr$_6$@C.

The amount of FA introduced into the pores of NU-1000 could be tuned by controlling the infiltration time. With increasing infiltration time from 12 h to 144 h, the BET specific area decreased (Figure 4.1), suggesting more PFA entered the pores with longer infiltration time. The BET specific surface area of each PFA@NU-1000 sample is shown in Table 4.1.
The surface area value for PFA@NU-1000-144h decreased dramatically compared to other PFA@NU-1000 samples, implying that most of the pores of NU-1000 were occupied by PFA, or the NU-1000 particles were covered by extra PFA on the outside.
Figure 4.1. (a) N₂ sorption isotherms of NU-1000 before and after infiltration with furfuryl alcohol (FA) vapor for the indicated lengths of time and polymerization of FA at 250 °C for 6 h. (b) Characteristic isotherms of different porous structures (adsorption curve: red; desorption curve: blue). Due to capillary condensation which often occurs in mesopores, the gas molecules condense into a liquid-like phase during adsorption. This strong intermolecular interaction leads to the desorption happening at a lower pressure compared to where the adsorption starts, resulting in the formation of a “hysteresis loop”. The shape of the hysteresis loop is related to the pore shapes. Image (b) was reproduced with permission from ref. \(^{340}\). Copyright (2018), Research Institute of Petroleum Exploration & Development, PetroChina. Published by Elsevier B.V.
Table 4.1. Textural and compositional data of NU-1000, infiltrated NU-1000 materials, and the corresponding pyrolyzed materials (600 °C).

<table>
<thead>
<tr>
<th>sample</th>
<th>BET area (m²/g)</th>
<th>pore volumeᵃ (cm³/g)</th>
<th>mesopore volumeᵃ (cm³/g)</th>
<th>composition C:Zrᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>NU-1000</td>
<td>2127</td>
<td>1.42</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>PFA@NU-1000-12</td>
<td>1707</td>
<td>1.10</td>
<td>0.99</td>
<td>15.8:1.0</td>
</tr>
<tr>
<td>Zr₆@C-12</td>
<td>287</td>
<td>0.17</td>
<td>0.07</td>
<td>11.1:1.0</td>
</tr>
<tr>
<td>PFA@NU-1000-24</td>
<td>1558</td>
<td>0.97</td>
<td>0.86</td>
<td>16.7:1.0</td>
</tr>
<tr>
<td>Zr₆@C-24</td>
<td>295</td>
<td>0.17</td>
<td>0.07</td>
<td>13.1:1.0</td>
</tr>
<tr>
<td>PFA@NU-1000-48</td>
<td>1035</td>
<td>0.76</td>
<td>0.70</td>
<td>24.1:1.0</td>
</tr>
<tr>
<td>Zr₆@C-48</td>
<td>350</td>
<td>0.22</td>
<td>0.11</td>
<td>15.5:1.0</td>
</tr>
<tr>
<td>PFA@NU-1000-72</td>
<td>805</td>
<td>0.57</td>
<td>0.56</td>
<td>25.7:1.0</td>
</tr>
<tr>
<td>Zr₆@C-72</td>
<td>266</td>
<td>0.16</td>
<td>0.08</td>
<td>16.4:1.0</td>
</tr>
<tr>
<td>PFA@NU-1000-144</td>
<td>131</td>
<td>0.20</td>
<td>0.19</td>
<td>ndᶜ</td>
</tr>
<tr>
<td>Zr₆@C-144</td>
<td>425</td>
<td>0.46</td>
<td>0.40</td>
<td>ndᶜ</td>
</tr>
</tbody>
</table>

ᵃ Pore volume was calculated using the non-local density functional theory, N₂ at 77 K, cylindrical model. A cutoff of 2 nm was used to determine the mesopore volume.

ᵇ Calculated through the combination of TGA data and CHN analysis data.

c nd = Not determined, because of the large excess of carbon in these samples.
The crystalline features of PFA@NU-1000s were examined by XRD (Figure 4.2a). Most of the peaks in NU-1000 were observed in PFA@NU-1000, indicating that the MOF structure was preserved after the infiltration and polymerization of FA. One difference among the profiles of various PFA@NU-1000 is the relative intensity of the (100) peak. The \( d \)-spacing for this peak corresponds to the spacing of the hexagonal channels (~3 nm) in NU-1000. With increasing infiltration time, the intensity of this peak decreased, as a result of contrast matching between the MOF and PFA in the large mesopores.

In order to further elucidate the distribution and location of the infiltrated PFA in NU-1000, difference envelope density (DED) analysis based on synchrotron X-ray diffraction data was performed on PFA@NU-1000 (Figure 4.2b; the -48h and -72h samples were tested). By calculating the difference between the electron densities in pristine NU-1000 and infiltrated NU-1000, DED maps were generated and provided an average distribution of PFA in NU-1000.\(^{341}\) It was observed that the PFA in PFA@NU-1000-72h (C/Zr ratio = 25.7, Table 4.1) occupies both hexagonal and triangular pores, as well as the pockets that are formed by four organic linker molecules between \( \text{Zr}_6 \) clusters. Additionally, the filler produces continuous excess electron density in the mesopore channels. For PFA@NU-1000-48h with less filling (C/Zr ratio = 24.1, Table 4.1), the electron density of infiltrated PFA becomes more localized in the large mesopores. These results suggested that the FA molecules infiltrated all types of the vacancies (hexagonal pores, triangular pores, and pockets) and accumulated in the large hexagonal pores with increasing infiltration time. For comparison, in a previous study by our group on introducing silica into NU-1000, the silica was found to be mainly in the hexagonal pores. In addition, a large portion of the
silica was located near the Zr$_6$ clusters, suggesting some affinity between the two phases (both are polar). The nonpolar PFA, in contrast, sits in the middle of either the hexagonal or the triangular pores.

Figure 4.2. (a) XRD patterns of NU-1000 before and after infiltration with FA vapor for the indicated lengths of time and polymerization of FA at 250 °C for 6 h. (b) Difference envelope density map of PFA@NU-1000-72h and -48h viewed from different projections. The pink colored regions correspond to the electron density differences between each sample and NU-1000. They are projected onto the NU-1000 structure.

4.3.2 Density Functional Theory Pore Size Distribution of PFA@NU-1000

Density functional theory (DFT) pore size distribution is a useful tool for the analysis of pore structures. It is derived from equations combining experimental isotherm data and theoretical isotherms, also named as kernels. A suitable DFT theory and some properties of the pore structures are needed as the prerequisites for the kernel calculation, such as the
pore shape, adsorbate and the adsorbent types. The commercial Quantachrome AsiQWin software has built-in DFT kernels for the calculation of pore size distribution. For the DFT theory, there are two options, non-local-DFT (NLDFT) and quenched solid DFT (QSDFT). NLDFT assumes that the surface of the adsorbent is smooth and homogeneous while QSDFT considers the effect of surface heterogeneity. After deciding on the analysis theory, one can set the pore shape as slit, cylindrical, or spherical shape, the adsorbate type as N\textsubscript{2}, CO\textsubscript{2}, or Ar, and the adsorbent type as carbon, silica, or zeolite. To generate an appropriate and reasonable plot of pore size distribution, it is important to set those conditions correctly.

In previous research on NU-1000, the pore size distribution was often generated using the conditions of N\textsubscript{2} at 77 K, NLDFT, slit pore, and carbon surface. However, considering the pore structure of NU-1000 and the shape of the hysteresis loop from its isotherm (Figure 4.1), it is more reasonable to apply a cylindrical pore model. A full comparison between different kernels with various conditions is shown in Figure 4.3. The pore size distribution graphs generated with different variables show mainly two peaks, representing the two types of pores (3.1 nm and 1.1 nm) in the NU-1000 structure, although they each have variations from the theoretical values. A shift of the peak corresponding to the large pore was observed in all the models with increasing amount of PFA inside the pores. In contrast, no shift of the peak corresponding to the 1.1 nm pore was observed, which was not consistent with the DED results demonstrated earlier. This was possibly due to the quadrupole moment of nitrogen molecules as the isotherm probe. When nitrogen molecules are used as adsorbates, especially in the micropore regions (< 2 nm), their
orientation is influenced by the chemical structures of the absorbent surfaces, which creates an uncertainty up to 20% in the cross-sectional area of the nitrogen molecules and leads to confusion in the generated isotherms. Another thing to notice was that the NLDFT, cylindrical, carbon and NLDFT, slit, carbon kernels generated unwanted peaks between the two major peaks, while the other three did not. This was possible because the QSDFT and the NLDFT, silica conditions described the adsorbent surface more accurately (QSDFT assumes heterogeneity of the adsorbent surface; NLDFT, silica assumes that the nitrogen molecules are adsorbed onto the oxide sites), implying that the nitrogen molecules interact more with the zirconium oxide clusters than with the organic linkers during adsorption.
Figure 4.3. Scheme of the NU-1000 structure and DFT pore size distributions of NU-1000 and PFA@NU-1000 samples generated with different kernels. These graphs are derived based on N$_2$ isotherm at 77 K with different models. NLDFT and QSDFT are the DFT calculation theories; cylindrical (cyl.) and slit are the pore shapes; carbon and silica are the absorbent types.

Considering that Ar gas is the preferred probe for the analysis of micropores, Ar isotherms at 87 K were obtained to understand how the micropores are filled as a result of infiltration with PFA. Unlike N$_2$, Ar does not possess a quadrupole moment and hence does not exhibit specific interactions with surface functional groups, which leads to a straightforward correlation between pore size/shape and pore filling pressure. Ar
adsorption at 87 K fills narrow micropores at significantly higher relative pressures in comparison with nitrogen at 77 K, which shortens equilibration times and permits the measurement of high resolution adsorption isotherms. The DFT pore size analysis reveals a clear decrease in microporosity for both PFA@NU-1000-48h and PFA@NU-1000-72h samples (Figure 4.4), consistent with the DED results. Additionally, it showcased more PFA in the micropores with longer infiltration hours. It is interesting to note that in the analysis of Ar sorption isotherms of PFA@NU-1000 samples, the application of a siliceous model in the DFT calculations resulted in better fits of the isotherms than a carbon model, both assuming cylindrical pores. This may be an indication of significant Ar–oxide interactions, implying that Ar could access the Zr₆ clusters in the infiltrated MOF. The choice of model (siliceous vs. carbonaceous) affects mainly the interpretation of micropore filling, because here pore filling is strongly influenced by the type of adsorptive-adsorbent surface interactions as well as pore geometry. In the case of mesopores, the adsorption sites/pore walls are already occupied with a mono- or multilayer of adsorbate prior to capillary condensation, and hence the effect of adsorptive-adsorbent surface interaction on the isotherm is reduced.
Figure 4. DFT pore size distributions of NU-1000 and NU-1000 infiltrated with different precursors with (a) QSDFT, siliceous model and (b) QSDFT, carbon model derived with Ar adsorption at 87 K.

4.3.3 Structural Characterization of the Zr₆@C Nanohybrids

Zr₆@C, as the nanohybrid product of the carbon nanocasting process, was derived from pyrolysis of PFA@NU-1000 at 600 °C for 1 h under N₂. XRD patterns of the Zr₆@C samples were relatively featureless and did not show any distinct X-ray peaks (Figure 4.5). In particular, no crystalline ZrO₂ phase was observed, which contrasts with pyrolyzed NU-1000, where broad reflections of nanosized tetragonal zirconia are observed in the XRD pattern. This difference indicated that the PFA mitigated the aggregation of Zr₆ clusters into larger ZrO₂ nanoparticles during pyrolysis. Based on the C/Zr ratio in Table 4.1, the Zr₆@C nanohybrids have a very high Zr content. For example, Zr₆@C-48h and -72h samples have 29.5 wt% and 28.5 wt% of Zr, respectively.
Figure 4.5. XRD patterns of pyrolyzed NU-1000 and Zr₆@C samples. The pyrolysis temperature was 600 °C.

The preservation of isolated Zr₆ clusters in the Zr₆@C samples after pyrolysis was further confirmed by PDF analysis (Figure 4.6, Zr₆@C-48h was used for the analysis). After subtracting the pattern of a reference sample (pyrolysis of a mixture of PFA and H₄TBAPy linker) from that of the Zr₆@C sample, two pronounced peaks centered at 2.15 and 3.41 Å were observed, which are associated with the Zr–O and Zr…Zr atom-atom distances, respectively. The fitted simulated pattern corresponds to 0.6 nm (69 wt%), 0.8 nm (27 wt%), 2.5 nm (0.4 wt%) ZrO₂ species as well as 1.7 nm (3.6%) graphitic species,
which indicates that most of the Zr$_6$ clusters were still intact (the Zr$_6$ cluster in original NU-1000 MOF has the size around 0.6 nm).
Figure 4.6. PDFs for Zr@C-48h and a reference carbon sample (the reference sample was prepared by pyrolyzing a mixture of PFA and the organic linker H₂TBAPy), dPDF, for Zr@C sample showing Zr–O and Zr…Zr correlations after subtracting the signals from the carbon phase and a simulated PDF pattern for a mixture of oxozirconium clusters (0.6 nm cubic, \(a = 4.88\ \text{Å} \ (69\ \text{wt\%})\) and larger cubic (0.8 nm, cubic, \(a = 4.88\ \text{Å} \ (27\ \text{wt\%})\) and 2.5 nm cubic, \(a = 4.88\ \text{Å} \ (0.4\ \text{wt\%})\) ZrO₂ and 1.7 nm graphitic species (3.6 wt\%)). Residuals at short range are attributed to distortion of the idealized Zr₆ clusters⁶⁴ and the fact that the carbon matrix still contained some hydrogen and oxygen groups that could not be perfectly described by the graphitic phase used in the simulation.
The morphology of the Zr$_6$@C samples was studied by SEM. The Zr$_6$@C retained the rod shape of the original NU-1000 (Figure 4.7). The BET specific surface area and the pore volume of the Zr$_6$@C samples are summarized in Table 4.1, showing that the Zr$_6$@C materials still maintained high porosity. One thing to note is that Zr$_6$@C-144h has a larger surface area than its precursor PFA@NU-1000-144h, which is different from the trends of other Zr$_6$@C materials. A big portion of its large surface area is attributed to mesopores in the carbon generated from the pyrolyzed PFA.
Figure 4.7. SEM images of (a) NU-1000, (b) Zr$_6$@C-12h, (c) Zr$_6$@C-24h, (d) Zr$_6$@C-48h, (e) Zr$_6$@C-72h, and (f) Zr$_6$@C-144h.

The structure of carbon in the final product was investigated by Raman spectroscopy. Two prominent peaks were observed in the Raman spectra of Zr$_6$@C samples (Figure 4.8). The peak at ~1351 cm$^{-1}$ (D-band) is associated with the A$_{1g}$ breathing mode of carbon rings in graphitic structures, and the one at ~1597 cm$^{-1}$ (G-band) originates from the E$_{2g}$ vibration.
mode. The G-band is commonly seen in graphitic carbon materials whereas the D-band only appears when there is structural disorder. Another broad peak at around 2800 cm\(^{-1}\) (2D-band) was observed, which exists in all types of sp\(^2\) carbon materials. On the basis of Raman spectra, a combination of disordered and graphitic carbon structures was present in the Zr\(_6\)@C nanohybrid. This result is consistent with previous studies on the pyrolysis of PFA, which exhibited that the furan rings in PFA chains fracture and gradually convert into graphitic structures while being heated at 500 °C. Notably, the linkers from the NU-1000 template consist of aromatic pyrene units also contribute significantly to the carbon content of the pyrolyzed product.
Figure 4.8. Raman spectra of different Zr$_6$@C samples. The G-band is associated with sp$^2$ carbon in the graphitic regions of the materials (in-plane bond-stretching motion of pairs of sp$^2$ carbon atoms). The D-band is associated with a vibrational mode arising from defects in the graphitic structure and is typically found in disordered carbon materials.\textsuperscript{347, 351} The schemes of the vibration modes were reprinted with permission from ref.\textsuperscript{347}, Copyright (2000), American Physical Society.

4.3.4 Accessibility of the Clusters in the Zr$_6$@C Nanohybrids

To be an efficient heterogeneous catalyst, the catalytically active species must be accessible to the potential reactants. Therefore, it is meaningful to check the accessibility of the Zr$_6$ clusters in the Zr$_6$@C material. For this purpose, pyridine adsorption was applied to test cluster accessibility via the Lewis acidity of the Zr$_6$ clusters.\textsuperscript{135} Pyridine is a commonly used probe molecule for the detection of acidic sites on metal oxide surfaces. Due to the lone electron pair on the nitrogen atom, pyridine can either coordinate to Lewis
acidic sites or be protonated by Brønsted acidic sites. As a result, the vibrational modes of pyridine are altered, causing shifts in the vibrational frequencies observed in the FT-IR spectrum.352

The FT-IR spectrum of Zr₆@C (Zr₆@C-48h) that had been exposed to pyridine shows a pronounced peak at 1436 cm⁻¹,353 associated with the vibration of the free pyridine ring (Figure 4.9a). However, no evidence for pyridine bound to Lewis acidic sites was offered, possibly due to the clusters shielded by the carbon network. To test this hypothesis, the Zr₆@C-48h sample was heated in static air at 300 °C for 30 min to remove some of the carbon and expose the Zr₆ clusters more. For the resulting material, two IR peaks associated with the vibration of the pyridine molecules bonded to the Lewis acid sites were observed,135 confirming that the post-treatment had made the Zr₆ clusters more accessible (Figure 4.9b). Additionally, when ammonia was used instead as a smaller probe molecule in temperature-programmed desorption (TPD) experiments, a TPD signal associated with Lewis acidic sites was observed (Figure 4.9c), confirming accessibility of the clusters to ammonia. One point to note is that Zr₆@C with higher carbon content, such as Zr₆@C-72h is likely to have poorer accessibility due to smaller surface area and pore volume.
Figure 4.9. (a) FT-IR spectra of Zr$_6$@C-48h before and after pyridine adsorption experiments. This sample had not been treated in air at 300 °C. (b) FT-IR spectra of Zr$_6$@C-48h sample heated in air at 300 °C for 30 min before (black) and after exposure to pyridine (red) and a difference spectrum of the two spectra (blue). (c) Ammonia TPD data for a NaY zeolite, an H-BEA zeolite, and Zr$_6$@C-48h. NaY was used as a reference sample with mainly Lewis acid sites and H-BEA as one with mainly Brønsted acid sites. Zr$_6$@C-48h shows the peak corresponding largely to Lewis acid sites, confirming the accessibility of ammonia molecules to the cluster sites.
The Raman spectrum of the sample that had first been heated in air shows an increase in the relative intensity ratio of the D-band to the G-band compared to the original Zr₆@C sample (Figure 4.10a), indicating the loss of some graphitic structures from partial oxidation of the carbon network. The rod-like particle morphology was maintained after this treatment, and no obvious difference was noticed in their dimension sizes (Figure 4.10b, c). In order to visually determine the presence of Zr₆ clusters, TEM images of microtomed Zr₆@C-48h and post-treated Zr₆@C-48h samples were obtained (Figure 4.10d, e). No extended aggregation of clusters was noticed, suggesting that the Zr₆ clusters remained intact during the heat treatment. These results suggest a possible method of increasing the cluster accessibility in the carbon-nanocast MOFs. However, the conductivity of the product would also be compromised during this process.
Figure 4.10. (a) Raman spectra of Zr$_6$@C-48h sample before and after 300 °C treatment in air (30 min). The ID/IG ratio increased from 2.53 to 2.87 after the heat treatment. SEM and TEM images of Zr$_6$@C-48h sample before (b, d) and after 300 °C treatment in air for 30 min (c, e).
4.3.5 Conductivity of the Zr₆@C Nanohybrids

As suggested in the introduction, a major goal of developing carbon–metal or metal oxide nanohybrids is for electrocatalysis. Therefore, it is important to test the conductivity of the developed carbon–oxozirconium cluster nanohybrid. For this purpose, electrochemical impedance spectroscopy (EIS) was performed on the Zr₆@C (Zr₆@C-72h) sample to measure its conductivity (Table 4.2). The conductivity of Zr₆@C as prepared was too low to measure. However, when the sample was heated further to 800 °C (Zr₆@C-800), the conductivity increased to 0.41 S/m. Interestingly, this value is lower than the conductivity of NU-1000 pyrolyzed at 800 °C, possibly due to the oxygen introduced by the furfuryl alcohol precursor during the nanocasting. Notably, the XRD pattern of the Zr₆@C-800 material remained featureless, suggesting that the clusters remained isolated (Figure 4.11).
Table 4.2. Conductivities of the Zr$_6$@C and control samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (S/m)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrolyzed NU-1000 (600 °C)</td>
<td>too low to measure</td>
</tr>
<tr>
<td>pyrolyzed NU-1000 (800 °C)</td>
<td>2.13</td>
</tr>
<tr>
<td>pyrolyzed mixture of PFA and linker</td>
<td>2.47</td>
</tr>
<tr>
<td>Zr$_6$@C-600</td>
<td>too low to measure</td>
</tr>
<tr>
<td>Zr$_6$@C-800</td>
<td>0.41</td>
</tr>
</tbody>
</table>

* The conductivity $\sigma$ was calculated using the equation $R = \frac{L}{\sigma A}$. Here, $R$ is the resistance, derived from the impedance spectrum, $L$ the thickness and $A$ the cross-sectional area of the pellet.

Figure 4.11. XRD patterns of the Zr$_6$@C-72h samples prepared by being heated to different temperatures (from bottom to top are 600 °C, 700 °C, 800 °C, respectively).
Raman spectra of the Zr$_6$@C and pyrolyzed NU-1000 samples (Figure 4.12) showed a decrease in the peak ratio $I_D/I_G$ with increasing pyrolysis temperature as the carbon matrix became more graphitic, consistent with the increase in conductivity observed by EIS. The reasonably high BET area (270 m$^2$/g) and pore volume (0.3 cm$^3$/g) of the Zr$_6$@C-800 sample indicate that the material remained porous after the high temperature treatment.

Figure 4.12. Raman spectra of Zr$_6$@C and pyrolyzed NU-1000 samples. The $I_D/I_G$ peak ratios are 2.83 for pyrolyzed NU-1000-800, 3.52 for pyrolyzed NU-1000-600, 2.67 for Zr$_6$@C-800, and 2.85 for Zr$_6$@C-600.\textsuperscript{146}
4.4 Conclusion

In this chapter, the development of a new carbon nanocasting method in NU-1000 was discussed. The extra carbon introduced into the system from furfuryl alcohol effectively avoided the aggregation of Zr$_6$ clusters during the pyrolysis, which resulted in the formation of a carbon–oxozirconium cluster nanohybrid (Zr$_6$@C). The developed nanohybrid material had relatively high porosity, and abundant and even-sized metal oxo clusters. The influence of the carbon nanocasting procedures on product structure was studied in detail. During infiltration, the furfuryl alcohol precursor entered both hexagonal and triangular pores of NU-1000 according to DED analysis and Ar sorption data. After pyrolysis, preservation of the Zr$_6$ clusters was confirmed by XRD and PDF analysis. The carbon phase in the Zr$_6$@C product was determined by Raman spectroscopy to be a combination of disordered and graphitic carbon. The accessibility of the Zr$_6$ clusters was tested by pyridine adsorption and ammonia TPD experiments. It was demonstrated that the Zr$_6$ clusters in the as-prepared Zr$_6$@C material were accessible to ammonia but not to pyridine. The accessibility of the Zr$_6$ clusters could be enhanced by heating the Zr$_6$@C material in air to partially remove the carbon.

The development of this type of nanocomposite material opens a gate for synthesizing other interesting carbon nanohybrids. For example, it was mentioned in the introduction that Cu$_2$O clusters can be grown onto Zr$_6$ clusters.$^{336}$ Cu$_2$O species are vital in an important industrial process, the partial oxidation of methane to produce methanol.$^{354-356}$ This reaction has been commonly performed through thermal catalysis at a relatively high temperature. A lot of effort has been dedicated to developing alternative electrocatalytic
pathways for this reaction. However, no commercialized method has been achieved in the past 100 years. Following the path of synthesizing Zr6@C, it is possible to fabricate a new carbon–Cu2O cluster nanohybrid, which potentially can show high catalytically activity towards the partial oxidation of methane because of the abundant uniform-sized active sites.

The conductivity of the current products is not high but could possibly be further increased by optimizing the infiltrating precursors, preferably introducing elements such as nitrogen or boron that are known to increase the conductivity of graphitic carbon. Additionally, the method described in this work could also potentially work on other MOFs.
Chapter 5

Synthesis of 3-Dimensionally Ordered Macroporous Tungsten and Investigation of its Temperature-Dependent Mechanical Behavior

Parts of this chapter were reprinted with permission from “Temperature-dependent Mechanical Behavior of Three-dimensionally Ordered Macroporous Tungsten” by Schmalbach, K. M.; Wang, Z.; Penn, R. L.; Poerschke D.; Antoniou A.; Stein A.; Mara N. A. J. Mater. Res. 2020, 35, 2556-2566.

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This work was done in collaboration with Prof. Nathan Mara and Kevin M. Schmalbach (performing frustum testing, micropillar compression, and related data analysis), Prof. R. Lee Penn, Prof David Poerschke (providing discussions on the materials synthesis and characterization) of University of Minnesota, and Prof. Antonia Antoniou (providing discussions on the mechanical testing results) of Georgia Institute of Technology.
5.1 Introduction

Starting from this chapter, the topic will shift from MOFs to another type of porous solid—three-dimensionally ordered macroporous (3DOM) materials. 3DOM materials, also known as inverse opals, are a type of cellular material typically fabricated through colloidal-crystal templating. They are known for possessing isotropic, highly ordered, continuous, and tunable porous structures with nanosized ligaments. Many types of materials have been synthesized as 3DOM structures, e.g., polymers, C, SiO$_2$, TiO$_2$, V$_2$O$_5$, Ni, Cu, W, W-Mo, etc. Due to their unique structural features and plentiful compositional varieties, 3DOM materials have been extensively studied in many different applications. In addition to their best-known usage as photonic crystals, 3DOM materials have shown potential in other fields, e.g., catalysis, sensing, fuel cells, batteries, supercapacitors, etc.

Given their unique structural properties and extensive chemical applications, there has been more interest in understanding the mechanical properties of 3DOM materials. This is important because one needs to know whether the materials are robust enough to be used in certain conditions. To date, the mechanical properties of several types of 3DOM materials have been studied, including polymers, metals, ceramics, and carbon.

The concept of cellular materials has been discussed in Chapter 1. In addition to 3DOM materials, some other well-known cellular materials include foams, lattice materials, honeycomb materials, etc. (Figure 1.4). In Figure 5.1a one can see how a typical 3DOM structure is constructed with many cell units. There have been several papers studying how
the 3DOM structures behave under pressures.\textsuperscript{193, 197, 199, 217, 369} Toivola et al. investigated the response of a 3DOM silica material under indentation (Berkovich indenter).\textsuperscript{197} They found that the 3DOM silica deformed via initial cell wall fracture followed by pore collapse. Do Rosário et al. later investigated the detailed stress distribution in 3DOM structures through finite elemental modeling.\textsuperscript{199} Their work demonstrated that the arch-like structures in 3DOM materials (\textbf{Figure 5.1b}) played an important role during compression. Those arch-like structures mitigated the stress concentration and dissipated it into surrounding areas. A similar conclusion was drawn by Cho et al., who found that the “necking arch” regions in a 3DOM SU-8 polymer material accommodated the most stress during compression through pore shape transformation, from sphere to ellipsoid.\textsuperscript{369}
Figure 5.1. (a) A scheme showing different types of pores in a 3DOM structure. Adapted with permission from ref.\textsuperscript{368}, Copyright (2013), WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Distribution of stress on a 3DOM structure. The figure was generated using finite element modeling. Adapted with permission from ref.\textsuperscript{369}, Copyright (2015), WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

As more is known about the mechanical properties of 3DOM materials, the interest has been growing on optimizing their structures and compositions to tune their mechanical properties. For example, there has been research investigating how pore sizes affect the mechanical properties of 3DOM materials.\textsuperscript{198, 368} Li et al. studied the relationship between
the mechanical properties of 3DOM Ni and its pore size over a wide range (from 312 nm to 1200 nm). They found that both hardness and elastic modulus of 3DOM Ni increased with decreasing pore size. A similar conclusion was drawn from the research done by Zhang et al., who found that a 3DOM poly(D, L-lactide-co-glycolide) material had an enhanced compressive modulus with smaller pore size. This was likely due to the increased amount of arch-type units in a certain compression volume with smaller pore size.

In terms of the windows in 3DOM structures, Zhang et al. observed that narrower windows helped increase the compressive modulus of a 3DOM polymer material. Interestingly, Chen et al. managed to prepare a 3DOM fluorinated polyimide material without any windows. They found that this windowless 3DOM fluorinated polyimide exhibited 1.7× elastic modulus and 5.2× hardness compared to the traditional 3DOM fluorinated polyimide. The reason behind this is likely that 3DOM structure is closer to a closed-cell structure (in which the cells are enclosed by their walls and not connected to other cells) with narrower windows. However, one should consider that fully closed cells prohibit mass transfer, which will limit the application ranges of such 3DOM materials.

Another efficient approach to enhance the mechanical properties of 3DOM materials is adjusting their chemical compositions. Due to their high surface areas and connective pore structures, 3DOM materials have easily accessible surfaces that could be modified. For example, Shetty et al. demonstrated that the mechanical properties of a 3DOM Ni material could be greatly enhanced when it underwent aluminization and had a new strengthening phase Ni₃Al formed in the ligaments. In their study, the elastic modulus
and hardness were increased by 17.6% and 81.6% after the aluminization process. Do Rosário et al. found that after a 3DOM SiO$_2$ material was coated with a thin layer of amorphous TiO$_2$, the elastic modulus and hardness of the overall materials were increased by 275% and 600%. Interestingly, it is also possible to etch off the original ligaments in 3DOM materials after they are coated. For example, Pikul et al. coated the surfaces of 3DOM Ni with alumina through atomic layer deposition, and then etched away the original Ni component. In this case, a new type of 3DOM alumina material with hollow ligaments was obtained.

Although many works have been done studying the mechanical properties of various 3DOM materials, the number of publications on this topic is still significantly smaller than that on studying their chemical properties and applications. There are many fundamental but important questions to answer, e.g., how the mechanical properties of 3DOM materials change with different temperatures, ligament sizes, or ligament crystallinity?

In this chapter, the mechanical properties of a 3DOM tungsten (3DOM W) material are investigated. Tungsten is a body-centered cubic (BCC) metal with high strength. BCC metals are known to possess highly temperature-dependent mechanical properties due to increasing numbers of active slip systems at elevated temperatures. Their mechanical properties are most drastically affected in the region around the brittle–ductile transition temperature (BDTT). The brittle–ductile transition (BDT) is an important consideration for structural materials; neglecting the BDT can have disastrous effects, such as the famous catastrophic hull failures of steel Liberty Ships during World War II.
We present in this chapter the synthesis of 3DOM W materials through two different polymethyl methacrylate (PMMA) colloidal crystal templates, fabricated through sedimentation and convective self-assembly. The sedimentation method was modified based on a protocol of synthesizing 3DOM W previously published by our group. The advantages of each method and optimization of synthetic methods are discussed. Finally, the mechanical behavior of 3DOM W across the BDT was investigated to assess the effects of increasing plasticity on the mechanical behavior of BCC metals in the 3DOM structure.

5.2 Experimental

5.2.1 Materials

The following chemicals were used as-received: 2,2'-azobis(2-methylpropionamidine) (>99%), methyl methacrylate (99.9%), tungsten monocrystalline powder (>99.9%, 0.6–1 micrometer sizes) from Aldrich Chemical Company; glacial acetic acid (ACS grade) from VWR International; hydrogen peroxide (certified ACS, 30%) from Fischer Chemical; methanol (ACS reagent, >99.8%) from Sigma-Aldrich; hydrogen gas (industrial grade) and argon gas (ultra high purity/zero grade) from Matheson.

5.2.2 Synthesis

Synthesis of the PMMA colloidal crystal templates. PMMA spheres with an average diameter of 397 ± 4 nm were synthesized by emulsifier-free emulsion polymerization following established methods. These spheres were assembled either into monolithic
pieces by gravity sedimentation or thin films by convective self assembly. For gravity sedimentation, a 15 wt% aqueous dispersion of the PMMA spheres was placed in a crystallization dish and allowed to settle for several weeks. Monolithic PMMA colloidal crystals gradually formed at the bottom of the crystallization dish as the spheres settled and the dispersion dried. For convective self-assembly, a silicon wafer with dimensions of 1.5 cm × 3.0 cm was placed vertically into a 10 mL beaker. A 1 wt% aqueous PMMA sphere dispersion was then added into the beaker, partially immersing the silicon wafers. The bottom of the beaker was heated to 65 °C. A PMMA colloidal crystal film formed on the silicon wafers as the water evaporated. Typically, a 2-cm long assembly formed in 3 h.

Synthesis of 3DOM W. Two types of 3DOM W materials were synthesized. One was denoted as monolithic 3DOM W, prepared from monolithic PMMA templates. The other one was denoted as 3DOM W film, prepared from PMMA thin films. The synthesis of monolithic 3DOM W was carried out following a previously reported method, using acetylated peroxotungstic acid (APTA) as the tungsten precursor. 3DOM W films were prepared by infiltrating the PMMA thin film templates with APTA solution and then heating the material under H₂ to remove the PMMA template and reduce the precursor to metallic tungsten. Detailed procedures are: using a syringe, a 1 M solution of APTA in a mixture of water and methanol (4:1 in volume) was injected to one end of the PMMA colloidal film template on the Si wafer. The precursor gradually diffused to infiltrate the whole template. Any excess precursor solution was wiped off with Kimtech wipes, and the film was allowed to dry in air for 12 h. This procedure was repeated in some cases when multiple infiltrations were needed. Then, the infiltrated PMMA colloidal template was
processed by heat treatment under H₂ at 1 atm (2 °C/min to 310 °C, remaining at 310 °C for 2 h, then 5 °C/min to 800 °C, remaining at 800 °C for 1 h). The resulting 3DOM W pieces had lateral dimensions ranging from 50 to 200 μm, with thicknesses between 5 to 20 μm, depending on the sample.

5.2.3 Characterization

Powder X-ray diffraction patterns were collected using a PANalytical X’Pert Pro diffractometer. The X-rays were generated with a Co anode (Kα radiation, λ = 1.789 Å) operating at 45 kV accelerating voltage, 40 mA emission current. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409 instrument. Samples were heated in air at a ramp rate of 5 °C/min. Scanning electron microscopy (SEM) was performed using a JEOL-6500 field emission scanning electron microscope with an accelerating voltage of 5.0 kV. All samples were coated with a 50 Å platinum film prior to SEM imaging.

Pillars with a diameter of 10 μm and an aspect ratio of approximately 2 were machined using an annular milling procedure on a FEI Helios G4 UX dual beam FIB/SEM. All cuts were performed with an accelerating voltage of 30 kV and ion current of 9.1 nA. Initial annuli with an inner diameter of 22 μm were cut prior to decreasing the annuli size to 13 μm. Final polishing cuts to reduce taper and achieve final diameter were performed at ion currents of 1.2 nA.
5.2.4 Frustum Testing

Thin films of 3DOM W were mounted with M-Bond 610 adhesive (Vishay Micro-Measurements, Malvern, PA) to the silicon wafer for frustum indentation. To minimize the amount of adhesive absorbed by the material, the substrate was heated to ~150 °C prior to application of the adhesive and allowed to partially cure prior to addition of 3DOM W pieces. The adhesive was then cured at 175 °C for 1 h. The samples were compressed in situ in a FEI Helios G4 UX dual beam FIB/SEM using a Hysitron PI88 Picoindenter (Bruker Nanosurfaces, Minneapolis, MN) equipped with an xR High Load Transducer and a 10 µm diameter diamond flat punch tip with a 60° cone angle. The films were compressed in displacement control with displacement rates of 20 nm/s.

The mean contact pressures were quantified using the method of Liu et al. The mean contact pressure is the load divided by the contact area of the indenter, assuming that the pressure is homogeneous under the indenter tip. In cases where the indenter tip overhung the edge of the sample, the contact area was calculated by:

\[ A_c = \frac{a^2}{2(Q - \sin(Q))}, \quad 0 < x < a, \]

where \( Q = 2 \cos^{-1}(|x - 1|) \), \( a \) is the indenter contact radius, and \( x \) is the fractional indenter overhang. An overhang of \( x = 1 \) corresponds to half of the indenter being in contact with the sample and half overhanging, whereas \( x = 0 \) is full contact such that \( A_c = \pi a^2 \). In this study, the dimensionless overhang ranged from 0 to \( \frac{3}{4} \); the majority of tests were performed with \( x \leq \frac{1}{2} \). In addition, the displacement is normalized by the contact radius of the indenter tip to achieve a dimensionless displacement.
5.2.5 Micropillar Compression

Monolithic 3DOM W pieces were mounted to a silicon wafer with PELCO high temperature carbon paste (Ted Pella, Redding, CA). A thin layer of paste was spread on the wafer prior to addition of 3DOM W pieces. The paste was cured at 90 °C for 2 h, then 260 °C for 2 h. Samples were compressed in situ in a FEI Helios G4 UX dual beam FIB/SEM using a Hysitron PI88 Picoindenter (Bruker Nanosurfaces, Minneapolis, MN) equipped with an xR Low Load Transducer and a 20 µm diameter diamond flat punch tip with 60° cone angle. Pillars were compressed in displacement control at engineering strain rates of approximately $5 \times 10^{-4}$ s$^{-1}$. Stresses were calculated by dividing the load by the cross-sectional area of the top of the pillar. This part and the frustum testing were performed by Kevin M. Schmalbach from the Mara group, Department of Chemical Engineering and Materials Science, UMN. More details can be found in our published paper.\textsuperscript{381}

5.3 Results and Discussion

5.3.1 Synthesis of PMMA Templates

To fabricate 3DOM W materials, two types of PMMA colloidal crystal templates were used. One was prepared through gravity sedimentation of PMMA spheres from its colloidal suspension.\textsuperscript{201} The other type was obtained through convective self-assembly of PMMA spheres onto silicon wafers.\textsuperscript{377} In the sedimentation process, the PMMA colloidal spheres gradually settled from the solution to the bottom of the container and were packed into a
monolithic colloidal crystal (Figure 5.2). The sedimentation method produced PMMA monoliths with sizes from millimeters up to centimeters (monolithic PMMA template).

Figure 5.2. Schematic showing the major synthetic processes. (a) Monolithic PMMA templates were fabricated using gravity sedimentation. (b) PMMA film templates were fabricated using convective self-assembly. (c) In both cases, the PMMA templates were infiltrated with a tungsten precursor solution, and the composite was converted to 3DOM W through reductive heating under H\(_2\) (2 °C/min to 310 °C, remaining at 310 °C for 2 h, then 5 °C/min to 800 °C, remaining at 800 °C for 1 h).

In the convective self-assembly, a silicon wafer as the substrate was inserted vertically into the PMMA colloidal suspension (Figure 5.3a). The container was heated at the bottom,
creating a convective colloid flux in the suspension. As water evaporated, the colloids at the substrate–solvent–air interface settled and assembled into an ordered linear structure on the substrate via lateral capillary force. With continuous heating, more colloids were drawn to the initially pinned colloids and gradually formed a colloidal crystal thin film (PMMA film template, Figure 5.2b). Notably, some major cracks were always seen in the products synthesized using the convective self-assembly. Longitudinal cracks formed due to the tensile forces during water evaporation, and transverse cracks occurred at the boundaries of wet and dry regimes as the water level decreased. These cracks broke the colloidal crystals into individual strips (Figure 5.3b). In this study, the strip-form PMMA templates and the resulting 3DOM W products are still referred to as “films”.

Figure 5.3. (a) A photo showing the experimental setup for convective self-assembly. A silicon wafer was placed vertically in a PMMA colloidal suspension. The beaker was heated at the bottom at 65 °C. (b) A photo showing the derived PMMA colloidal crystal films. The longitudinal cracks could be seen, which broke the film into separate strips. The smallest scale in the image is 1 mm. (c) SEM image of a small area on one strip, showing that the PMMA colloidal spheres aligned orderly.
The film templates had large areas of well-aligned PMMA colloids (Figure 5.3c). However, the quality of the thin films greatly depended on the heating temperatures and the colloid concentration. A rather high temperature, e.g., more than 80 °C would cause the water to evaporate too fast so that the colloids did not have enough time to adjust their positions and align in an orderly fashion. The PMMA templates synthesized in this way had more disordered regions (Figure 5.4). The concentration affected the overall morphology of the colloidal crystal. Discontinuous colloidal crystal films were achieved with low concentrations (typically < 0.3 wt%), which was likely due to the insufficient colloid flux during the growth of the colloidal crystal films. In contrast, thick films with wavy surfaces and no opalescence were achieved with high concentrations (typically > 2 wt%), which was likely because too many colloids precipitated at the same time and assembled poorly. The conditions used in the current study were 1 wt% PMMA suspension heated at 65 °C. The achieved PMMA films had uncracked strips with lengths around 0.5 cm, widths around 0.2 cm, and thicknesses less than 50 μm.
Figure 5.4. SEM images of PMMA colloidal crystal films prepared using 1 wt% PMMA colloidal suspension at 65 °C, (a) and 93 °C, (b). More disordered regions could be observed on the film prepared at 93 °C, especially at the bottom left area in the image.

5.3.2 Synthesis of 3DOM W

3DOM W was synthesized through the infiltration of APTA as a tungsten precursor into PMMA colloidal crystal templates followed by reductive heat treatment in H$_2$ atmosphere. Either 3DOM W monoliths or 3DOM W films were obtained using the corresponding PMMA template (Figure 5.2c). Dwelling at 310 °C helped with the removal of the PMMA templates. Further heating in the H$_2$ atmosphere enabled the formation of W via reduction of the WO$_3$ generated from the condensation of APTA. XRD patterns of both the 3DOM W film and monolithic 3DOM W indicated that the material contained α-tungsten (BCC) as its only crystalline phase (Figure 5.5).
Extensive volume shrinkage was observed during processing of 3DOM W (Figure 5.6d), because the majority of the APTA precursor consisted of solvent (water and methanol), which left the system during the heat treatment. To increase the fraction of the APTA in the PMMA template and reduce the occurrence of voids, multiple cycles of APTA infiltration and drying were performed. For monolithic 3DOM W (synthesized from the monolithic PMMA template), multiple infiltrations increased the uptake of APTA molecules and resulted in larger regions of well-defined 3DOM structure as remaining...
voids were filled with additional precursor material (Figure 5.6). However, for more than three infiltrations, the monolithic PMMA templates were inclined to crumble into smaller pieces.

**Figure 5.6.** SEM images of fragments from 3DOM W monoliths synthesized using (a) one, (b) two, or (c) three steps of APTA infiltration into the colloidal crystal templates. (d) TGA curves for PMMA monoliths that had been infiltrated with APTA once, twice, or three times. The experiments were performed in air. To determine the W mass% in the infiltrated monolithic PMMA templates, it was assumed that the final product was WO₃. The inset photos show the size change from the starting material, infiltrated monolithic PMMA template to the product, monolithic 3DOM W.
For the synthesis of 3DOM W films (from PMMA film templates), multiple infiltrations generated a tungsten overlayer resulting from excess APTA precursor (Figure 5.7). Therefore, monolithic 3DOM W pieces prepared by triple infiltration and 3DOM W films prepared by a single infiltration were employed for the subsequent studies.

Figure 5.7. SEM images taken at different magnifications of 3DOM W films synthesized using two APTA infiltration attempts. A W overlayer formed and covered the surface of the 3DOM structure.

Compared to monolithic 3DOM W, the 3DOM W film exhibited much larger ordered domains (Figure 5.8), making them suitable to study a less defective microstructure via frustum indentation, as described in the following section. The different degrees of order in the 3DOM structures were attributed to the different preparation methods of the PMMA templates. The convective self-assembly method can generate much thinner layers of packed PMMA spheres with uniform thickness compared to the sedimentation method. The thinner PMMA template contains fewer mispacked PMMA spheres, and it is more controllable during the infiltration of precursor, which avoids over- or insufficient infiltration.
Figure 5.8. SEM images with different magnification of a 3DOM W monolith, (a, b) and a 3DOM W film, (c, d). The 3DOM W film contained larger regions of well-defined and ordered structure. Both 3DOM W materials had window openings of ~226 nm (determined by measuring the distance between inner sides of the parallel ligaments in one hexagonal unit).

Because the PMMA film templates were already thin and had small, continuous domains, the resulting 3DOM W films were even smaller pieces with lateral dimensions in the range of 50–200 μm, thicknesses between 5 and 20 μm, and ligament widths of 35–40 nm (Figure 5.9). The thickness of the 3DOM W films was not suitable for the milling of micropillars of sufficient size to ensure a large enough representative volume. The
dimensions of monolithic 3DOM W pieces made them suitable for large micropillars as well as other experiments dealing with larger-scale measurements.

**Figure 5.9.** SEM images of a 3DOM W film piece at different areas. The lateral dimensions of this piece were around 100 μm and 390 μm, (a). The thickness varied across the piece from 8 μm on the left, (b) to 16 μm on the right, (c), and the ligament width was 35–40 nm, (d). Most 3DOM W film pieces had lateral dimensions ranging between 50 and 200 μm.

The pore size was kept constant in this study for the films and monoliths. However, as mentioned in the introduction, the pore size was expected to influence the mechanical
behavior of 3DOM materials. By employing PMMA colloids with different sizes, 3DOM W materials with different pore sizes were achieved (Figure 5.10). Such effects will be studied in future research.

**Figure 5.10.** SEM images of 3DOM W films prepared using differently sized PMMA colloids. The window sizes (the distance between inner sides of the parallel ligaments in one hexagonal unit) were measured to show the differences between different materials. The synthesized 3DOM W materials have window sizes of 260 nm, (a); 226 nm, (b); 181 nm, (c); 164 nm, (d). The material in (b) was the one used in this study.
5.3.3 Frustum Indentation of 3DOM W

3DOM W films were employed for frustum indentation. Videos were taken during the experiments, and frames from the failure points at 30 °C, 125 °C, and 225 °C were shown in Figure 5.11a, b, and c, respectively. The corresponding Eulerian strain maps and morphology of the deformed areas after indentation are shown in Figure 5.11d, e, f and Figure 5.11g, h, i (the Eulerian strain is a type of strain measured according to certain pre-chosen reference points in the system). At 30 °C, the strain was localized in the vicinity of the indenter tip, indicating minimal stress redistribution in 3DOM W at this temperature (Figure 5.11a, d). When the temperature was elevated to 125 °C (Figure 5.11b, e) and 225 °C (Figure 5.11c, f), strain fields emanated from the indenter tip to a larger volume, indicating that the failure occurred on a more global scale with some delocalization of stress to surrounding ligaments. This conclusion was supported by the images of the deformed area after indentation. At 30 °C, the material ultimately conformed to the shape of the indenter tip during the deformation process (Figure 5.11g). In contrast, the strain field became more distributed at higher temperatures (Figure 5.11h, i) with large pieces of material sheared off from the bulk structure.
Figure 5.11. Images from in situ frustum compression of a 3DOM W film. Scale bar indicates 5 µm. (a–c) Images from compression at which failure occurs, i.e., when a major crack can be seen in the structure. (d–f) Eulerian strains in the vertical direction ($\varepsilon_y$) at the point just before a major crack is apparent in the 3DOM structure. Multiple small regions were used as the reference points to track the movement of the interesting areas. (g–i) Morphology of residual indent after frustum indentation.

Profile traces on the Eulerian strain map along the centerline of the indenter axis (Figure 5.12) were used to provide a more representative comparison of the strain distribution underneath the center of the indenter. At 30 °C, the maximum compressive strain along the centerline of the indenter was approximately 0.024. In contrast, maximum compressive strains were nearly an order of magnitude higher at 125 °C (0.25) and 225 °C (0.21), indicating a large increase in deformability between 30 and 125 °C. This increase
in ductility could be attributed to an increase in plasticity, possibly caused by the activation of additional slip systems at higher temperatures.\textsuperscript{374}
Figure 5.12. Profile of Eulerian strains at 30 °C, (a); 125 °C, (b); 225 °C, (c). The inset images are the Eulerian strain maps just before major cracks. The curves show the corresponding strains ($\varepsilon_{yy}$) at different y-positions (along the centerline of the indenter axis).
Analysis of the contact pressure as a function of the normalized displacement (Figure 5.13a) enabled further quantitative comparison of the deformation behavior at 30, 125, and 225 °C. The curves shown in Figure 5.13a were selected to be representative due to best contact conditions at the start of the experiment. The increase in mean contact pressure with increased displacement is likely a result of the densification of the material underneath the indenter tip.
Figure 5.13. Quantification of mean contact pressures from in situ frustum indentation. (a) Mean contact pressure for selected tests as a function of temperature. Tests were selected based on the flattest indenter-sample contact. h/a is the normalized displacement or non-dimensional displacement, in which h is the displacement into the sample, and a is the contact radius. (b) A focused view of the initial loading of the tests in a) up to the point of failure, indicated by the ‘×’ symbol. (c) Mean contact pressure at the point of failure, i.e., when a crack formed in the material, as a function of deformation temperature.
Since the stress state changed significantly after a large-scale fracture had occurred, the focus was put on analyzing the pre-fracture behaviors of the 3DOM W material at different temperatures (Figure 5.13b). The slopes of the initial loading regions ($h/a < 0.17$) for 30 °C and 125 °C experiments were very close, indicating a consistent behavior at the initial compression stage for 3DOM W materials heated to lower than 125 °C. However, the 125 °C experiment failed at a much larger displacement value ($h/a \sim 0.4$) than the 30 °C one. The difference suggested that plastic deformation of the 3DOM W ligaments was limited at 30 °C, and the materials tended to deform by ligament fracture. This fracture-dominated behavior of the ligaments also applies to the material heated to 125 °C at lower contact pressure. At higher contact pressure, there was likely enough stress to nucleate new dislocations in the ligaments, so they could plastically deform rather than break. In other words, the 3DOM W heated to 125 °C exhibited a mixed behavior between fracture and plasticity under increasing contact pressure.

For the 3DOM W heated to 225 °C, the slope of the initial loading region was significantly higher. It was likely due to the presence of more energetically favorable slip systems at higher temperature (body-centered cubic materials like tungsten are known to have multiple active slip planes). Under this situation, the dislocation sources in 3DOM W ligaments could be feasibly oriented for nucleation, resulting in the ability of the overall material to plastically deform at a rather small stress. In contrast, fewer planes were able to actively slip at lower temperature, leading to an increased brittle-fracture behavior under pressure.
Based on the mean contact pressure–displacement plot, one could also compare the
energy absorbed by the 3DOM W material during the deformation process, which was
directly related to the area underneath the curve. It was found that approximately 6 times
more mechanical energy was absorbed by the 3DOM W at 125 °C, and 18 times more at
225 °C compared to that at 30 °C. This was likely due to the increased plasticity of the
ligaments as temperature was elevated.

The mean contact pressure at the failure points for 3DOM W materials at different
temperatures is shown in Figure 5.13c. At 30 °C, the mean contact pressure at the time of
failure was very low; the W ligaments appeared to fracture at relatively low stresses in the
absence of large-scale plasticity. In contrast, the stresses at failure were nearly a factor of
2 higher at 125 °C and nearly an order of magnitude higher at 225 °C. The higher sustained
contact pressure at failure was likely due to delocalization of stress to other ligaments rather
than fracture of ligaments.

Through these experiments, it was possible to infer that the 3DOM W material
underwent a brittle-ductile transition with increased temperatures. At 30 °C, the local
behavior under the indenter tip appeared to be mostly brittle, whereas significant plasticity
was observed at 225 °C. It could be concluded that a brittle-ductile transition began
somewhere below 125 °C. As a comparison, Gumbsch et al. found the brittle-ductile
transition temperature (BDTT) of single crystal tungsten ranging from 97 °C to 197 °C.242
Considering the polycrystalline nature of the ligaments, 3DOM W seems to have relative
similar BDTT as single crystal tungsten. However, more experiments would be required to
draw a precise conclusion.
5.3.4 Micropillar Compression of 3DOM W

To further investigate the mechanical property–structure relationships for 3DOM W, a micropillar compression test was employed. A video alongside the compression process was acquired, from which a frame demonstrating the failing moment of a micropillar of monolithic 3DOM W was shown in Figure 5.14a. Compared to 3DOM W films, extended voids and disordered regions could be seen within the structure of monolithic 3DOM W. Based on the video, a stress–strain curve for the monolithic 3DOM W was generated (Figure 5.14c).
Figure 5.14. Micropillar compression of monolithic 3DOM W. (a) Failure of pillar due to buckling caused by voids at the bottom of the pillar; (b) Eulerian strain map ($\varepsilon_{yy}$) of pillar during compression showing compaction bands; (c) Engineering stress-strain curve for the compression of the micropillar in (a). The pillar yield stress could be read to be around 50 MPa

Based on the digital image correlation analysis, a strain map of the micropillar prior to the failure was generated (Figure 5.14b). The alternating bands shown in the strain map
are compaction bands, which are characteristic of deformation of porous solids with relatively low densities. This feature indicated that the 3DOM W material behaved like a foam under pressure, which allowed Gibson–Ashby model to be applied for further analyzing the structure. The model employed here was developed by Pikul et al. using finite elements simulations of a 3DOM Ni structure assuming isotropic elasticity (equation 1), in which $\sigma^*$ is the measured yield strength of the pillar, $\sigma_y$ is the yield strength in the ligament, and $\frac{\rho^*}{\rho_s}$ is the relative density, i.e., the density of the 3DOM material divided by the density of bulk, non-porous tungsten.

$$\sigma^* = 0.78\sigma_y \left( \frac{\rho^*}{\rho_s} \right)^{1.52}$$

Using a relative density ($\frac{\rho^*}{\rho_s}$) of 5 % and a pillar yield stress ($\sigma^*$) of 50 MPa (Figure 5.14c), the ligament yield stress ($\sigma_y$) was calculated to be 6.1 GPa. For comparison, the yield stress of a 200 nm single crystalline tungsten pillar was found to be 3.5 GPa along the [001] direction and 2 GPa along the [235] direction. (This is not a perfect comparison since the 3DOM W was polycrystalline, so the two materials might deform by different mechanisms, as discussed in Chapter 1. However, this is the closest case known to the author of this thesis). The high yield stress of 3DOM W material might come from a combination effect of the structure geometry and the nano-sized ligament. However, more experiments would be needed to draw a complete conclusion.
5.4 Conclusion

In this chapter, the synthesis of two types of 3DOM W materials was discussed, including 3DOM W monoliths and 3DOM W films. They were fabricated based on two types of PMMA colloidal crystal templates, synthesized through sedimentation and convective self-assembly. The optimization of both methods was investigated, attempting to achieve large-area and ordered 3DOM regions with few defects or cracks. The 3DOM W films were found to have flat surfaces and larger domains of uncracked 3DOM regions, making them suitable for the study on a less defective microstructure. In contrast, the 3DOM W monoliths had larger overall representative volumes for relatively large-scale measurements, such as the micropillar compression tests.

After achieving these morphologies, the mechanical behaviors of 3DOM W across the brittle-ductile transition were studied. Micropillar compression tests on 3DOM W monoliths at 30 °C revealed structural failure at a contact pressure of around 50 MPa, and ligament yield strengths on the order of 6.1 GPa. In situ frustum indentation of 3DOM W films showed low contact pressures before failure at 30 °C, but nearly an order of magnitude increase at 225 °C. Compressive strains on the order of 2% were seen at 30 °C under the center of the indenter tip, whereas 20% was seen at both 125 and 225 °C. The plastic deformation of the 3DOM structure at 225 °C allowed for nearly 18 times mechanical energy absorption than at 30 °C. Increased plasticity of the ligaments was observed as temperature was elevated, which indicated that the 3DOM W material underwent a brittle-ductile transition with increased temperature. The starting point should be somewhere lower than 125 °C. The temperature-dependent enhancement in properties
exhibited in this 3DOM W system may be exploited further for engineering applications in other low-density structures with small ligament lengths.
Chapter 6

Development of 3D Periodic and Interpenetrating Tungsten–Silicon Oxycarbide Nanocomposites for Mechanical Robustness

This work was done in collaboration with Prof. Nathan Mara and Kevin M. Schmalbach (performing nanoindentation and related data analysis), Prof. R. Lee Penn, Prof David Poerschke (providing discussions on the materials synthesis and characterization) of University of Minnesota, and Prof. Antonia Antoniou (providing discussions on the mechanical testing results) of Georgia Institute of Technology. The preceramic polymer precursor SMP-10 was provided by Prof. David Poerschke.
6.1 Introduction

Nanocomposites are solid materials with multiple phases, in which one of the phases has at least one dimension less than 100 nm, or the structure has repeated nano-scale distances between different phases. Compared to the corresponding monolithic materials, many properties of nanocomposites are improved, such as thermal stability, electrical conductivity, catalytic activities, and mechanical properties. Classic and well-studied examples are metal–ceramic nanocomposites, which show the ability of combining the merits of metals and ceramics, namely ductility (metals) and toughness (ceramics), with high strength. Metal–ceramic nanocomposites have exhibited exceptional mechanical properties that are not achievable in monolithic metals or ceramics, which make them valuable for applications in fields such as the aerospace and automotive industries.

In addition to the mutual enhancement of components in the nanocomposites, the nanosized features also greatly influence their mechanical properties. As discussed in section 1.3.1, the size–strength relationship in single-component materials has been extensively studied, with the “smaller is stronger” paradigm observed in single-crystal, polycrystalline, and amorphous materials. In the best-understood polycrystalline metal systems, the number of grain boundaries increases with decreasing grain size, creating high energy barriers to dislocation motion, thus increasing the yield strength of the materials according to the well-known Hall–Petch relationship, following a relationship, where d is the critical dimension such as grain diameter. For composites with nanoscale-sized components, the “smaller is stronger” phenomena has also been observed. Different from single-component nanomaterials, a
special interface-driven strengthening paradigm occurs in nanocomposites. The abundant interfaces between components in nanocomposites enhance their mechanical properties by acting as sources, sinks, barriers, or storage sites for dislocations active in the metal phase.\textsuperscript{226, 398-399} Additionally, the mechanical response of the composite can be tuned by controlling the degree of bonding between the phases. Strong interfacial bonding is shown to increase the toughness of metal–matrix composites (MMCs) with an isotropic microstructure,\textsuperscript{236-237, 400} while weak bonding is preferred in many brittle matrix, fiber-reinforced composites to allow for mechanical decoupling between the fiber and matrix.\textsuperscript{401-402}

Metal–ceramic nanocomposites are traditionally synthesized by mixing the precursors (e.g., ball milling and co-precipitation), then converting them into nanocomposites under high pressure or high temperature (e.g., pressureless sintering, spark-plasma sintering, hot pressing, and cold consolidation).\textsuperscript{403-407} One drawback of these synthetic routes is the lack of control over the microstructures. Multilayer metal–ceramic nanocomposites are a relatively new but well studied type of metal–ceramic nanocomposites.\textsuperscript{225-226} Their microstructures can be controlled rather precisely with layer thickness less than 5 nm through physical vapor deposition, such as magnetron sputtering and ion beam sputtering.\textsuperscript{235, 397, 408} However, these materials have anisotropic properties, which limits their range of application. In this context, well-designed microstructures are desired for further development of metal–ceramic nanocomposites, that can potentially enhance the overall mechanical properties of the materials and provide more opportunity to study the
relationships between the nanoscopic structures and macroscopic mechanical properties of metal–ceramic nanocomposites.\textsuperscript{238-240}

In the present work, we introduce a novel method to fabricate metal–ceramic nano-interpenetrating composites (nano-IPCs) with periodic structures. IPCs are a relatively new type of metal–ceramic composite, having co-continuous three-dimensionally interpenetrating phases compared to traditional metal-matrix composites having discrete reinforcing phases. The development of IPCs provides the opportunity to achieve full functionality of the components and isotropic mechanical/physical properties.\textsuperscript{218, 228-230} A detailed introduction on IPCs can be found in section 1.4.1.

In our method, three-dimensionally ordered macroporous (3DOM) materials are applied to control the architecture of the IPC. As introduced in Chapter 1, 3DOM materials are porous solids that feature a highly ordered, fully interconnected, periodic porous structure with uniform pore sizes, typically a few hundred nanometers in diameter.\textsuperscript{203, 213} Having ordered and periodic structures with nanosized ligaments, 3DOM materials in certain compositions have exhibited high strength.\textsuperscript{193, 199-200, 381} Due to their interconnected porous structure, 3DOM materials are good candidates for synthesizing IPC type nanocomposites. To achieve this, another component can be introduced into the interconnected voids in 3DOM materials, followed by a specific solidification process. Several 3DOM material-based nanocomposites have been reported, such as 3DOM carbon–vanadia,\textsuperscript{205, 409} and 3DOM carbon–zeolite.\textsuperscript{410-411}

In this chapter, we demonstrate a synthetic approach to fabricate the metal–ceramic nano-IPC material 3DOM tungsten–silicon oxycarbide (W–SiOC), in which 3DOM W was
infiltrated with a polymer-derived SiOC ceramic phase. Tungsten, a body-centered cubic metal, was selected in part because it undergoes a brittle-ductile transition (BDT) in the range 100–200 °C.\textsuperscript{242} Notably, large increases in deformability have been observed in 3DOM W when the temperature was raised to 225 °C.\textsuperscript{381} This behavior facilitates mechanical characterization when both phases are brittle at room temperature, as well as when the tungsten exhibits increased plasticity at elevated temperatures.

SiOC polymer-derived ceramics are widely studied given their flexibility (compared to other ceramic processing methods) in the preparation of ceramic composites, fibers, and net-shape monolithic components.\textsuperscript{412-413} The liquid precursors can be cured in the range 200–400 °C to form soft (Young’s Modulus (E) < 1 GPa) polymers. Upon further heating, the organic-to-inorganic conversion (pyrolysis) produces an amorphous ceramic with increased stiffness (E \approx 150 GPa)\textsuperscript{414} containing fine-scale (typically nm to µm) porosity generated during the escape of gaseous hydrocarbons during pyrolysis.\textsuperscript{415} The as-pyrolyzed material is understood to have a nano-domain structure comprising Si-O-based regions surrounded by turbostratic or graphitic carbon.\textsuperscript{416} Heat treatment temperatures above 1200 °C are typically required to crystallize the SiOC. In addition to its processability, recent work has shown that mesoporous SiOC can sustain significant, recoverable elastic strains and ductile-like deformation.\textsuperscript{417} The hypothesis underpinning this work is that the integration of the ordered 3DOM W and porous SiOC will produce a resilient IPC type nanocomposite.

To prepare the 3DOM W–SiOC nanocomposite, 3DOM W was synthesized through colloidal crystal templating and applied as the starting scaffold (the 3DOM W in this
The chapter was the same as the 3DOM W film in Chapter 5, followed by infiltration with the preceramic polymer precursor SMP-10, a polycarbosilane. Through further heat treatment, the precursor SMP-10 condensed and formed a SiOC ceramic phase in the voids of 3DOM W. The 3DOM W–SiOC material consisted of continuous phases of crystalline tungsten and amorphous silicon oxycarbide, with some discrete free carbon. The 3DOM nanocomposite material featured a highly periodic structure, which remained thermally stable up to 1000 °C. Mechanical properties of the 3DOM W–SiOC material were investigated using micropillar compression tests in the temperature range from 30 to 575 °C. 3DOM W–SiOC showed a maximum stress of 1.1 GPa at 30 °C, a factor of 22 greater than for the 3DOM W matrix alone. The deformation mode of 3DOM W–SiOC exhibited a transition from fracture-dominated deformation at low temperature to plastic deformation above 425 °C.

6.2 Experimental

6.2.1 Materials

The following chemicals were used as-received: 2,2’-azobis(2-methylpropionamidine) (>99%), methyl methacrylate (99.9%), tungsten monocrystalline powder (>99.9%, 0.6–1 micrometer sizes) from Aldrich Chemical Company; glacial acetic acid (ACS grade) from VWR International; hydrogen peroxide (certified ACS, 30%), tetrahydrofuran (THF, certified ACS) from Fisher Chemical; methanol (ACS reagent, >99.8%) from Sigma-Aldrich; StarPCS™ SMP-10, a commercially available allyhydridopolycarbosilane polymer from Starfire Systems, Inc; PELCO® high temperature carbon paste from Ted
Pella, Inc; hydrogen gas (industrial grade) and argon gas (ultra-high purity/zero grade) from Matheson.

6.2.2 Synthesis of 3DOM W–SiOC Nanocomposites

*Synthesis of 3DOM W–SiOC.* A 3DOM W film (supported on a Si wafer) was used as the matrix for synthesizing the 3DOM W–SiOC material. Detailed procedures for synthesizing the 3DOM W film can be found in Chapter 5. Small amounts of SMP-10 were injected by a syringe to spots on the Si wafer next to 3DOM W pieces. The injected SMP-10 gradually diffused into the 3DOM W pieces. This step was repeated until all the 3DOM W pieces on the Si wafer were infiltrated with SMP-10. This procedure was designed to prevent 3DOM W pieces from floating on top of SMP-10 drops (floating 3DOM W pieces tended to agglomerate, which was undesirable for later mechanical tests). The mixture of 3DOM W and SMP-10 together with the supporting Si wafer was then transferred into a Schlenk flask. Further infiltration of SMP-10 into the 3DOM W was facilitated by applying a dynamic vacuum (200–500 torr) to the flask. The evacuation was continued for 1 h after the vacuum level had stabilized. The Si wafer with the mixture on it was then removed from the flask, and any excess SMP-10 was removed with Kimtech wipes. The infiltrated 3DOM W pieces (supported on the Si wafer) were then pyrolyzed under Ar (2 °C/min to 800 °C with no dwell time) in a graphite crucible to form the 3DOM W–SiOC composite material during pyrolysis. Tantalum foil was used as an oxygen getter to cover the graphite crucible. For multiple infiltrations, 50 vol% SMP-10/50 vol% THF was used as the precursor for the 2nd and 3rd infiltration steps; 30 vol% SMP-10/70 vol% THF was used as
the precursor for the 4\textsuperscript{th} and 5\textsuperscript{th} infiltration steps. The composite materials were pyrolyzed (2 °C/min to 800 °C under Ar) following each infiltration step. Some of the 3DOM W–SiOC materials were heated further to monitor structural and compositional changes at high temperature (1 °C/min to either 1000 °C or 1300 °C with no dwell time after reaching 800 °C).

6.2.3 Characterization

FT-IR spectra were obtained in both attenuated total reflectance (ATR) and transmission modes. The ATR-IR spectra were obtained using a Bruker Alpha-P Platinum FT-IR spectrometer equipped with a Platinum ATR sampling module hosting a diamond crystal (single bounce). The transmission IR spectra were obtained using a Nicolet Magna 760 IR spectrometer, using powdered samples compressed between a pair of NaCl windows. Raman spectroscopy was performed using a WITec Alpha300R confocal Raman microscope with 532.0 nm laser radiation, and the scattering was detected using a DV401 CCD thermoelectrically-cooled detector. Nitrogen sorption experiments were performed on a Quantachrome Autosorb-iQ2 analyzer using ultrahigh purity grade nitrogen as the adsorbate. All samples were degassed under dynamic vacuum (0.003 mTorr) at 120 °C for 12 h before analyses. Brunauer–Emmett–Teller (BET) surface areas were evaluated from the adsorption isotherms in the relative pressure range 0.01–0.20. Pore size distributions were obtained from nitrogen isotherms using nonlocal density functional theory (DFT) methods and assuming nitrogen adsorption at 77 K in slit-shaped carbonaceous pores. Powder X-ray diffraction patterns were collected using a PANalytical X’Pert Pro
diffractometer. The X-rays were generated with a Co anode (Ka radiation, λ = 1.789 Å) operating at 45 kV accelerating voltage and 40 mA emission current. Scanning electron microscopy (SEM) was performed using a JEOL-6500 field emission scanning electron microscope with an accelerating voltage of 5.0 kV. The fast-Fourier-transform (FFT) image analysis was performed via Gatan Microscopy Suite (GMS) software. Scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM-EDS) was conducted using a JEOL JXA-8900 electron probe microanalyzer equipped with an Ultradry-SDD detector and operating with an accelerating voltage of 10.0 kV to 15.0 kV. All samples were coated with a 50 Å platinum film prior to SEM imaging. Transmission electron microscopy (TEM) images were obtained using a FEI Tecnai T12 transmission electron microscope with an accelerating voltage of 120 kV and a LaB₆ filament. Samples were sonicated for 5 min in ethanol and then deposited onto carbon film-coated copper grids, and the solvent was allowed to evaporate under ambient conditions.

6.2.4 Nanoindentation

Preparation of specimen. The fabricated 3DOM W–SiOC pieces were transferred and mounted onto a steel AFM disk using PELCO® high temperature carbon paste. The specimen was then cured at 90 °C for 3 h and 270 °C for another 3 h (5 °C/min from 90 °C to 270 °C). Micropillars with a diameter of approximately 10 µm and an aspect ratio of 2 were produced via an annular milling protocol in a FEI Quanta 200 3D dual beam FIB/SEM using gradually reducing diameter annuli at an accelerating voltage of 30 kV and beam current of 5 nA. Final smoothing annuli were performed with a lower beam current of 1
nA to reduce taper and remove redeposited material to more clearly see the ligament structure for digital image correlation (DIC) analysis.

**Micropillar compression.** Samples were compressed in situ in a FEI Helios G4 UX dual beam FIB/SEM using a Hysitron PI88 Picoindenter (Bruker Nanosurfaces, Minneapolis, MN) equipped with an xR High Load Transducer and a 20 µm diameter diamond flat punch tip with 60° cone angle. Pillars were compressed in displacement control at displacement rates of 10 nm/s, corresponding to nominal engineering strain rates of approximately $5 \times 10^{-4}$ s$^{-1}$. After 1 µm of displacement, a partial unload was performed to obtain a pillar stiffness. Both the sample and indenter tip were heated to each testing temperature (30, 225, 425, and 575 °C) and allowed to thermally equilibrate for at least 30 minutes prior to compression testing. The data were corrected for load cell drift, substrate compliance, and contact point corrections. Stresses were calculated by dividing the load by the cross-sectional area of the top of the pillar, and strains were calculated as indenter displacement divided by the pillar height. The relative energies absorbed during deformation were calculated using the area under the stress–strain curve calculated via the Matlab *trapz* function, a trapezoidal numerical integration algorithm.

SEM images of the micropillar were processed using digital image correlation (DIC) to obtain in-plane strain maps. In DIC, the relative displacements in the deformed specimen were calculated based on comparison to reference (undeformed) images. The features inherent to the 3DOM structure provided sufficient contrast for the DIC algorithm to track points during the deformation process without the need for an applied speckle pattern. Videos recorded during the in situ compression of the 3DOM structure were separated into
individual frames. To shorten the processing time, every third frame was used without additional image post-processing. DIC analysis was performed using an open-source analysis algorithm (Ncorr). The applied subset radius was 150 nm, and the strain radius was 250 nm. This package was used to calculate the vertical normal strain ($\varepsilon_{yy}$) to determine the local strains during deformation. This part was performed by Kevin M. Schmalbach from the Mara group, Department of Chemical Engineering and Materials Science, UMN.

6.3 Results and Discussion

6.3.1 Synthesis of 3DOM W–SiOC Materials

The procedures for synthesizing the 3DOM W–SiOC materials are shown in Figure 6.1. Major cracks occurred naturally in the PMMA templates prepared through convective self-assembly, where longitudinal cracks formed because of the tensile forces generated during water evaporation, and transverse cracks formed at the boundaries of wet and dry regimes as the water level decreased. These cracks broke the colloidal crystals into individual strips (Figure 5.3b), which meant the final 3DOM W products were also individual strips (Figure 6.2a). A single strip of 3DOM W had well-defined and periodic 3DOM regions (Figure 6.2b) with window openings of ~226 nm between adjacent cages and ligament widths of ~30 nm (Figure 6.2c). The synthesized 3DOM W was in the body-centered cubic $\alpha$-W form (Figure 5.5).
Figure 6.1. Scheme summarizing the synthetic steps for fabricating 3DOM W–SiOC materials. PMMA spheres were first packed into colloidal crystals via convective self-assembly. The resulting PMMA colloidal crystals were used as a sacrificial template to fabricate 3DOM W materials. SMP-10 polymeric precursor was then introduced into the voids of 3DOM W, and pyrolyzed to form SiOC. The schematic of the final 3DOM W–SiOC material is based on the results of multiple characterization methods, which will be discussed in the following text.
Figure 6.2. SEM (a-e) and TEM (f) images of 3DOM W (a, b, c) and 3DOM W–SiOC (d, e, f) materials at different magnifications. The positions of some W ligaments, introduced SiOC, and some larger voids are marked in (d). Textural mesopores can be observed between the SiOC particles in (f). The FFT image as an inset in (b) was generated based on the selected area (10 μm × 10 μm) outlined by dashed lines; it confirms the periodicity of the 3DOM W structure in the viewing plane.
3DOM W–SiOC was synthesized by infiltrating the interconnected void space of 3DOM W with the polycarbosilane SMP-10, a preceramic polymeric precursor, followed by heat treatment under Ar. SMP-10 does not contain any oxygen, so theoretically it condenses and forms SiC during heat treatment. However, the oxygen was very difficult to avoid during the pyrolysis, which resulted in the formation of SiOC instead of SiC as the final ceramic phase (Figure 6.3). Although not as hard as SiC, SiOC materials have superior oxidation and corrosion resistance, especially at high temperatures. A detailed compositional analysis of the 3DOM W–SiOC is discussed in the next section.

Figure 6.3. SEM-EDS maps of the 3DOM W–SiOC material. Two separate sites were analyzed, with the determined atom% shown in the images. The final empirical formula was calculated to be W_{0.42±0.03}Si_{1.0±0.0}C_{1.8±0.2}O_{0.56±0.11} on the basis of the average composition from these sites.

The developed 3DOM W–SiOC material maintained the 3DOM structure (Figure 6.2d, e), with the SiOC component present inside the pores of 3DOM W in the form of granular particles (Figure 6.2d, f). Differently sized voids were present throughout the SiOC phase. The textural mesopores and cracks in SiOC shown in the TEM image (Figure
6.2f) were likely caused by the volume shrinkage during the conversion of liquid SMP-10 precursor to the solid SiOC phase. Extensive volume shrinkage has been observed in the preparation of polymer derived ceramics using preceramic polymer precursors. Typically, the volume shrinkage can exceed 50% and sometimes reaches up to 80% for certain type of polymer precursor.\textsuperscript{421-422} Differently sized pores and cracks are usually generated during the volume shrinkage. Additionally, some larger voids were observed in our material (Figure 6.2d). In addition to the influence of volume shrinkage, the formation of these large voids was possibly also due to incomplete SMP-10 precursor infiltration into certain regions of the porous tungsten scaffold prior to pyrolysis. Given that denser material could have better mechanical properties, multiple infiltrations of SMP-10 followed by pyrolysis were performed, attempting to introduce more SiOC into the system. However, on the basis of SEM images, no obvious improvement in pore filling was observed even after five cycles (each cycle refers to one-time infiltration followed by pyrolysis, Figure 6.4).
Figure 6.4. Scheme illustrating the fabrication of 3DOM W–SiOC materials with one to five infiltration cycles (each cycle refers to one-time infiltration with the corresponding precursor followed by pyrolysis). Pure SMP-10 was used for the infiltration in the 1\textsuperscript{st} cycle. A mixture of 50 vol\% SMP-10/50 vol\% THF was used for the 2\textsuperscript{nd} and 3\textsuperscript{rd} cycles. A mixture of 30 vol\% SMP-10/70 vol\% THF was used for the 4\textsuperscript{th} and 5\textsuperscript{th} cycles. SEM images of 3DOM W–SiOC obtained after one cycle (a), three cycles (b), and five cycles (c). No obvious differences were observed in terms of the pore filling.

To further study the evolution of pore structure during multiple infiltrations, N\textsubscript{2} physisorption analysis was applied (Figure 6.5). The original 3DOM W material exhibited a surface area of 26 m\textsuperscript{2}/g and a micro-/mesopore volume of 0.11 cm\textsuperscript{3}/g, mostly due to textural mesopores between tungsten grains in the skeletal walls.\textsuperscript{340} 3DOM W–SiOC produced after one infiltration cycle (3DOM W–SiOC-1cycle) had a similar surface area (88 m\textsuperscript{2}/g) and pore volume (0.11 cm\textsuperscript{3}/g) as 3DOM W-SiOC obtained after three infiltration cycles (3DOM W–SiOC-3cycles, with a surface area of 81 m\textsuperscript{2}/g and a pore volume of 0.10 cm\textsuperscript{3}/g). Different from 3DOM W, the shapes of the hysteresis loops in their isotherms suggested the presence of ink bottle-type pores in the 3DOM W–SiOC materials.\textsuperscript{340}
Moreover, the similar hysteresis loops of 3DOM W–SiOC-1cycle and 3DOM W–SiOC-3cycles indicated that multiple infiltrations did not introduce more precursor material into the macropores, possibly because the “necks” of the ink bottle-type pores were too narrow for the precursors to pass through. This idea was further supported by the density-functional theory (DFT) pore size distribution graphs, which revealed that 3DOM W–SiOC-1cycle and 3DOM W–SiOC-3cycles both possessed pores with similar size distributions and diameters centered around 4 nm. Therefore, 3DOM W–SiOC-1cycle was used for the following mechanical measurements. The overall porosity and density of the 3DOM W–SiOC-1cycle material (referred to as 3DOM W–SiOC in the following text) were calculated based on the isotherm data and component densities to be ~58% and 1.73 g/cm³.
Figure 6.5. (a) N$_2$ sorption isotherms of 3DOM W and 3DOM W–SiOC materials prepared using one or three infiltration cycles and (b) DFT pore size distribution of 3DOM W–SiOC-1cycle and -3cycles. The BET surface areas and pore volumes were calculated to be 26 m$^2$/g and 0.11 cm$^3$/g for 3DOM W, 88 m$^2$/g and 0.11 cm$^3$/g for 3DOM W–SiOC-1cycle, and 81 m$^2$/g and 0.10 cm$^3$/g for 3DOM W–SiOC-3cycles, respectively. Pore size distributions were calculated by non-local DFT using a slit pore model. The overall porosity and density of 3DOM W–SiOC-1cycle were calculated by resolving its empirical formula (W$_{0.42}$Si$_{1.0}$C$_{1.8}$O$_{0.56}$) into sub-phases: 0.42W (crystalline tungsten) + Si$_{1.0}$C$_{0.72}$O$_{0.56}$ (stoichiometric silicon oxycarbide, SiC$_{1-x}$O$_{2x}$) + 1.1C (free carbon). Considering that 3DOM W–SiOC was fabricated using 3DOM W as the matrix, the total volume (Vol) of 3DOM W–SiOC should satisfy the equation: Vol(3DOM W–SiOC) = Vol(3DOM W matrix) = Vol(W ligaments) + Vol(silicon oxycarbide) + Vol(free carbon) + Vol(micro and meso pores) + Vol(large voids). The volumes of different components in 3DOM W–SiOC were calculated on the basis of their relative mass percentages and bulk density values. The volume of 3DOM W matrix was calculated using a 5% relative density of tungsten determined in our previous study. As a result, the overall porosity and density of 3DOM W–SiOC were calculated to be 58% and 1.73 g/cm$^3$. 189
6.3.2 Investigation of the Composition and Structure of 3DOM W–SiOC

The empirical composition of 3DOM W–SiOC was determined to be \( W_{0.42}Si_{1.0}C_{1.8}O_{0.56} \) by SEM-EDS analysis (Figure 6.3). To further investigate the phases of the 3DOM W–SiOC material, selected area electron diffraction (SAED) (Figure 6.6) and powder XRD patterns (Figure 6.7) were obtained. The major crystalline phase was identified to be \( \alpha \)-W by both techniques. When the 3DOM W region was excluded from the selected area (Figure 6.6c), no evidence for crystalline SiC or SiO\(_2\) phases was observed in the SAED pattern, suggesting the presence of an amorphous SiOC phase.
Figure 6.6. TEM images and corresponding selected-area electron diffraction patterns of the 3DOM W–SiOC material. Three different areas were selected. Area (a) and (b) included the 3DOM W ligaments and the internal SiOC phase. Area (c) was selected to avoid any 3DOM W region.
Figure 6.7. XRD patterns of 3DOM W–SiOC prepared at 800 °C, and 3DOM W–SiOC, additionally heated to 1000 °C (zero dwell time). Both samples contained α-W as the only crystalline phase.

An interesting observation was evidence for the presence of β-W$_2$C crystalline phase in one of the SAED patterns (Figure 6.6a) but not in the XRD pattern (Figure 6.7), likely due to the low mass percentage of the W$_2$C phase in the overall 3DOM W–SiOC material. The occurrence of W$_2$C was likely attributed to the formed “free carbon” reacting with the nanosized W ligaments in some localized areas. Free carbon has been an important consideration in the research field of polymer-derived ceramics (PDCs). It is formed...
as a result of phase separation when the polymeric precursor is processed at elevated temperatures. Free carbon usually exists in the form of nanocrystalline graphitic domains. The free carbon formed during the processing of polymeric precursors can suppress further crystallization and phase separation in the PDC materials at higher temperatures by acting as a diffusion barrier. However, free carbon can also compromise the strength and hardness of PDC materials.

To confirm the possible presence of free carbon in the 3DOM W–SiOC materials, Raman spectroscopy was applied as a local and short-range probing tool. Multiple random areas of 3DOM W–SiOC were selected for the measurement (Figure 6.8). The characteristic D-band (around 1355 cm\(^{-1}\); only active with disorder in graphitic sheets and from edge regions) and G-band (around 1580 cm\(^{-1}\), originates from all sp\(^2\) carbon sites) for carbon were observed in the 3DOM W–SiOC samples. The intensities of the D- and G-bands varied at different areas, indicating that free carbon nanodomains were distributed non-uniformly throughout the 3DOM W–SiOC material (Figure 6.8a). The lateral size (\(L_a\)) of free carbon nanodomains (nanocrystalline graphite) can be calculated from the relative intensities of the D- and G-bands, \(I_D/I_G\). On this basis, the \(L_a\) of free carbon in 3DOM W–SiOC material was determined to be about 1.0 nm, based on the Raman spectrum with the most distinguished D- and G-bands (Figure 6.8b). Additionally, the appearance of W–C vibration peaks in some Raman spectra confirmed the reaction between W ligaments and free carbon in certain localized regions (Figure 6.8, Table 6.1).
Figure 6.8. (a) Raman spectra collected at several random areas of the 3DOM W–SiOC material. The D- and G-bands are characteristic peaks of free carbon (nanocrystalline graphite). Additionally, peaks corresponding to W–C vibrations were observed (694 cm$^{-1}$ and 802 cm$^{-1}$). The differences among the Raman spectra suggested that the free carbon nanodomains were not uniformly distributed throughout the material. Some additional peaks could not be assigned. Peak assignments in the literature for SiC, SiO$_2$, WC$_y$, WSi$_x$, and WO$_3$ are listed in Table 6.1. (b) Raman spectra of 3DOM W–SiOC and a 3DOM W–SiOC sample heated further to 1000 °C (zero dwell time). The insets show the fitting of D- and G-bands in the range from 900 to 1900 cm$^{-1}$. The four Gaussian peaks used for the deconvolution of the Raman spectra were positioned at 1200 cm$^{-1}$, 1340 cm$^{-1}$ (D-band), 1511 cm$^{-1}$, and 1591 cm$^{-1}$ (G-band). The peaks at 1200 cm$^{-1}$ and 1511 cm$^{-1}$ were chosen to represent the sp$^3$ carbon vibrations in free carbon.$^{351}$ The lateral size ($L_a$) was calculated based on the equation $I_D/I_G = C(\lambda)/L_a$, where $C(\lambda = 532.0 \text{ nm}) = 5 \text{ nm}$.$^{428}$
Table 6.1. Reported Raman peaks of the possible compositions in 3DOM W–SiOC material

<table>
<thead>
<tr>
<th>composition</th>
<th>reported Raman peaks</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>amorphous: 400, 750, 1350, 1600 cm⁻¹; crystalline: 796, 973 cm⁻¹</td>
<td>429</td>
</tr>
<tr>
<td>SiO₂</td>
<td>one sharp peak in the range of 400–530 cm⁻¹</td>
<td>430</td>
</tr>
<tr>
<td>WSiₓ</td>
<td>two major peaks: 331–333 cm⁻¹, 451–454 cm⁻¹</td>
<td>431-432</td>
</tr>
<tr>
<td>WCᵧ</td>
<td>two major peaks: 685–693 cm⁻¹, 800–807 cm⁻¹</td>
<td>433</td>
</tr>
<tr>
<td>WO₃</td>
<td>274, 327, 715, 805 cm⁻¹</td>
<td>434-435</td>
</tr>
</tbody>
</table>

The relative content of free carbon present in the 3DOM W–SiOC was estimated based on the empirical formula \((W_{0.42}Si_{1.0}C_{1.8}O_{0.56})\) derived from SEM-EDS (Figure 6.3). The formula of a stoichiometric SiOC material is \(SiO_{2(1-x)}C_x\), in which a tetravalent carbon atom can be replaced by two divalent oxygen atoms. Whenever free carbon is generated inside the SiOC material, the composition becomes \(SiO_{2(1-x)}C_x + yC\). Therefore, the approximate composition of the 3DOM W–SiOC material can be rewritten in more detail as \(W_{0.42}Si_{1.0}O_{0.56}C_{0.72} + 1.1C\).

Effort was also made to determine the state of oxygen in the developed 3DOM W–SiOC material. Typically, for the preparation of silicon oxycarbide, polysiloxanes are used as the polymeric precursors, and the O/Si ratio in the product is often in the range of 1.0 to 1.5. The precursor SMP-10 used in this study, however, does not contain oxygen elements. Therefore, the oxygen was likely introduced from the environment during the pyrolysis even though a tantalum getter was used to minimize the introduction of oxygen.
The possibility of oxygen forming crystalline phases such as WO$_3$ and SiO$_2$ was excluded by both long-range (XRD, Figure 6.7) and local (SAED, Figure 6.6; Raman, Figure 6.8) characterization techniques. In this context, FT-IR was applied alternatively to investigate another property, the bonding environment of the oxygen atoms in the 3DOM W–SiOC material (Figure 6.9). The dominant peaks in the ATR-IR spectrum for cured SMP-10 corresponded to C–H (3000–2800 cm$^{-1}$), Si–H (2117 cm$^{-1}$, and 931 cm$^{-1}$), Si–CH$_2$–Si (1035 cm$^{-1}$), Si–C (828 cm$^{-1}$), and Si–CH$_3$ (743 cm$^{-1}$) vibrations, respectively. These peaks disappeared in the ATR-IR spectra of pyrolyzed SMP-10 and 3DOM W–SiOC, suggesting the completion of polymer-to-ceramic conversion at 800 °C. Instead, remarkably increased intensities below 1100 cm$^{-1}$ were observed in the ATR-IR spectra of pyrolyzed SMP-10 and 3DOM W–SiOC, indicating that they both had Si–C vibration (centered at ~800 cm$^{-1}$) as the dominant vibration. Higher resolution transmission IR spectra (inset of Figure 6.9) revealed that, compared to the spectrum of pyrolyzed SMP-10 with a broad peak for Si–C vibration, the 3DOM W–SiOC spectrum exhibited extra peaks, corresponding to Si–O–Si (1100 cm$^{-1}$, and 468 cm$^{-1}$), and Si–C (801 cm$^{-1}$) vibrations. Therefore, the bonding environment of oxygen in the 3DOM W–SiOC was concluded to be mainly in the form of Si–O–Si.
Figure 6.9. FT-IR spectra of 3DOM W–SiOC, pyrolyzed SMP-10 (SMP-10 heated to 800 °C with a ramp rate of 2 °C/min in Ar), and cured SMP-10 (SMP-10 heated at 130 °C for 12 h in Ar) in ATR (4000–400 cm⁻¹) and transmission (inset, 1400–400 cm⁻¹) modes.

The thermal stability of the 3DOM W–SiOC composite was also investigated. At 1000 °C, the material maintained its 3DOM structure (Figure 6.10a) and α-W was still present as the only crystalline phase observed in the XRD pattern (Figure 6.7). However, more intense peaks corresponding to W–C vibrations were observed in the Raman spectrum (Figure 6.8b), suggesting the formation of more WCₓ species (either WC or W₂C) at
localized areas. Additionally, the lateral size of free carbon nanodomains increased from 1.0 nm to 1.3 nm on the basis of the calculated $I_D/I_G$ ratios. This result indicated the growth of free carbon at elevated temperature, possibly due to the continuing phase separation in the amorphous SiOC.

![SEM images](image)

**Figure 6.10.** SEM images of 3DOM W–SiOC heated to 1000 °C (zero dwell time) (a) and 3DOM W–SiOC heated to 1300 °C (zero dwell time) (b). The 3DOM structure was maintained at 1000 °C, but destroyed at 1300 °C due to extensive sintering.
At an even higher temperature of 1300 °C, the periodic 3DOM structure was destroyed, and a coral-like structure formed as a result of sintering (Figure 6.10b). Raman spectra were also collected at random areas to examine the possibility of further reaction between W (or WC\textsubscript{x}) and SiOC (Figure 6.11). Raman peaks corresponding to both W–Si and W–C vibrations were observed, suggesting the formation of WSi\textsubscript{x} and WC\textsubscript{x} at 1300 °C.\textsuperscript{431-433} Interestingly, strong carbon signals (D- and G-bands) were observed in some areas but not in others, which was likely caused by extensive phase separation or the loss of carbon (converted into CO) at this high temperature. Additionally, the lateral size of the free carbon nanodomains increased to 2.3 nm, which supported the idea that these tended to grow with increasing temperature.
Figure 6.11. Raman spectra collected at several random areas of the 3DOM W–SiOC heated to 1300 °C (zero dwell time). In addition to the D- and G-bands of free carbon, peaks were observed at 332 and 446 cm$^{-1}$ (W–Si vibration), as well as at 694 and 802 cm$^{-1}$ (W–C vibration). Some additional peaks could not be assigned. Peak assignments in the literature for SiC, SiO$_2$, WC$_y$, WSi$_x$, and WO$_3$ are listed in Table 6.1.
6.3.3 Thermomechanical Properties of 3DOM W–SiOC

Micropillars of 3DOM W–SiOC were compressed at temperatures ranging from 30 °C to 575 °C (Figure 6.12). A clear change in deformation morphology was observed as the temperature was increased. At 30 °C, a flaw on the surface of the pillar was generated under compression, which provided a stress concentration and allowed a crack propagating along the entirety of the pillar (Figure 6.12b). In this context, the material failed catastrophically in a brittle manner. At 225 °C, the 3DOM W–SiOC pillar failed in the way similar to that at 30 °C, with a crack propagating along the plane of maximum shear (Figure 6.12d). However, some branches of the major crack occurred, implying increased plasticity, but not enough to prevent the material from failing in a primarily brittle manner.
Figure 6.12. Before- and post-deformation SEM images of 3DOM W–SiOC pillars compressed at 30 °C (a, b), 225 °C (c, d), 425 °C (e, f), and 575 °C (g, h). The major deformation mode changes from fracture-dominated deformation at low temperatures to plastic deformation at higher temperatures.
A large change in deformability was observed at 425 °C (Figure 6.12f), where large pillar displacements, and hence strains, were accommodated in the deformation process. Instead of undergoing catastrophic failure as it was in the lower-temperature cases, the structure widened significantly towards the bottom of the pillar, indicating significant plasticity of at least one phase. A similar morphology was observed at 575 °C (Figure 6.12h), where the pillar widened during deformation, however, at the top rather than the bottom.

2D strain maps of the strain along the loading direction based on digital image correlation (DIC) analysis are shown in Figure 6.13. At 30 °C, local strains were relatively low prior to failure (Figure 6.13a), which was attributed to the brittleness of the 3DOM W–SiOC material at low temperatures. The local strain distribution was qualitatively the same at 225 °C (Figure 6.13b). However, at 425 °C and 575 °C, compaction (collapse) bands appeared in the local strain maps (Figure 6.13c, d), indicating that the material behaved in the manner of low-density solids at 425 °C and above.\textsuperscript{391} Such banding occurs when the dominant failure mode is plastic hinge formation of the W ligaments and typically becomes less evident with decreasing porosity, usually completely disappearing at porosities around 70%\textsuperscript{390,443} Here, the porosity was approximately 60%, thereby outside the conditions where compaction banding is commonly observed. This anomalous behavior poses two questions: 1) Why did compaction bands show up only at higher temperature? 2) Why did compaction bands show up in a low porosity material?
**Figure 6.13.** Maps of the vertical normal strain during compression of 3DOM W–SiOC micropillars at 30 °C (a), 225 °C (b), 425 °C (c), and 575 °C (d). Strains are fairly homogeneous at 30 °C and 225 °C, whereas horizontal bands of constant strain (compaction bands) are present at 425 °C and 575 °C, indicating behavior similar to a low-density solid.

In the previous study of the compression of 3DOM W micropillars, compaction bands occurred at room temperature (**Figure 5.14**), whereas they were not observed in 3DOM W–SiOC until 425 °C (**Figure 6.13**). This indicates that at relatively low temperatures, the limiting deformation mode changed from bending-dominated ligament deformation in the case of an open-cell (3DOM W) to the material-dependent fracture in the nanocomposite (3DOM W–SiOC). This was likely because only few slip systems were active in the W phase at low temperatures, making it difficult for the W ligaments to
plastically deform. The complex pore structure and surface anomalies of the non-W phases contributed to stress concentrations that eventually allowed for formation and propagation of unstable cracks. Additionally, the low fracture toughness of the SiOC phase exacerbated unstable cracking. Therefore, at temperatures below or near the brittle-ductile transition temperature (BDTT) of W ligaments (100–200 °C), cracks in the SiOC phase continued through the W ligaments with relative ease under compression. Once the temperature was elevated significantly beyond the BDTT of tungsten, the W ligaments yielded under bending, resulting in the formation of plastic hinges. Therefore, the cracks in the non-W phases could not propagate easily through the W ligaments anymore. In this context, 3DOM W–SiOC deformed as the plastic hinges collapsed, which generated the compaction bands. This behavior indicated that at temperatures much higher than the BDTT of tungsten, the plastic deformation of parent matrix, tungsten dominated the overall deformation mode of the 3DOM W–SiOC nanocomposite. Engineering stress–strain curves for 3DOM W–SiOC at 30 °C and 3DOM W at room temperature can be seen in Figure 6.14a. Compared to 3DOM W beginning to fail at approximately 50 MPa, 3DOM W–SiOC supported stresses as high as 1.1 GPa, a factor of 22 greater than 3DOM W. The significantly increased endured stresses was attributed to the addition of SiOC phase inside the pores of 3DOM W. Also due to the addition of SiOC, the 3DOM W–SiOC material deformed to a maximum of ~10% strain prior to catastrophic failure, whereas 3DOM W exhibited strains of greater than 15% without catastrophic failure.
Stress–strain curves for 3DOM W–SiOC at all temperatures are shown in Figure 6.14b. A general trend is the maximum stress decreasing and maximum strain increasing at elevated temperatures. The maximum stress and strain were 1.1 GPa, 10% and 0.8 GPa, 12% for the 3DOM W–SiOC pillars at 30 and 225 °C, respectively. This result indicated that a slight increase in the ductility of the 3DOM W–SiOC occurred at 225 °C, although the pillar still failed catastrophically as it was at 30 °C (Figure 6.12).

A significantly change happened when the 3DOM W–SiOC was compressed at 425 °C, where clear yield behavior was observed at only 0.3 GPa, followed by some hardening up to maximum stresses of ~0.6 GPa and maximum strains of ~25%, doubling that at 225 °C. Similar behavior was observed at 575 °C, where yield behavior was observed at 0.1 GPa, and maximum stresses were only ~0.2 GPa at large (~30%) strains, after significant geometric hardening, stemming from the increase in cross-sectional area in contact with the indenter (Figure 6.12g, h).
The energy absorbed by the materials during the deformation process was also investigated. It was derived by measuring the area under the stress-strain curve. The best energy absorber was found to be 3DOM W–SiOC at 425 °C. On average, it absorbed 1.52× more energy than at 30 °C, 1.79× more than at 225 °C, 2.38× more than at 575 °C, and 15.9× more than 3DOM W at room temperature. At lower temperatures (30 and 225 °C), the limited strain due to the brittleness of 3DOM W–SiOC resulted in low energy absorption. With higher temperature, deformability of the 3DOM W–SiOC material increased remarkably, leading to large strains but also small stresses. Therefore, although 3DOM W–SiOC at 575 °C had the largest strain, its small stress values finally resulted in lower energy absorption than even for the low temperature cases.

The developed 3DOM W–SiOC nanocomposite exhibited an extraordinarily high specific strength (640 MPa/(Mg/m³) at 30 °C), calculated based on its failure strength (1.1 GPa) and density (1.73 g/cm³). This specific strength value is significantly higher than those reported for other porous materials such as 3DOM W (52 MPa/(Mg/m³)), 3DOM nickel (220 MPa/(Mg/m³)), nanoporous tungsten (120-250 MPa/(Mg/m³)), and 3DOM SiO₂/TiO₂ composites (125-460 MPa/(Mg/m³)). Additionally, the specific strength of 3DOM W–SiOC remains high even at high temperatures, decreasing to 460 MPa/(Mg/m³) at 225 °C, 170 MPa/(Mg/m³) at 425 °C, and 58 MPa/(Mg/m³) by 575 °C (Figure 6.15). The specific strength of 3DOM W–SiOC at 30 °C and 225 °C are similar to that of carbon fiber-reinforced polymers. However, 3DOM W–SiOC is able to withstand significantly higher temperatures than a polymer-based composite while still retaining relatively high specific strength.
Figure 6.15. Ashby map showing relationship between strength and density using data from ref.\textsuperscript{445}. CRFP: carbon fiber reinforced polymer. Data points: 3DOM W–SiOC (squares, black to green increasing temperature, this study), NP W (triangles, black to green increasing relative density),\textsuperscript{444} SiO\textsubscript{2}/TiO\textsubscript{2} inverse opals (IO) (circles, black to green increasing TiO\textsubscript{2} thickness),\textsuperscript{193} Nickel inverse opals (IO) (star),\textsuperscript{200} 3DOM W (X).\textsuperscript{381}
6.4 Conclusion

In this chapter, a novel method to fabricate interpenetrating metal–ceramic nanocomposites was described. Using 3DOM W as a scaffold, liquid preceramic precursor SMP-10 was introduced into the pores of the 3DOM material, followed by condensation and pyrolysis to form the 3DOM W–SiOC material. This nanocomposite was composed of bicontinuous, periodic networks of crystalline $\alpha$-W and amorphous SiOC phases, also containing discrete free carbon nanodomains (nanocrystalline graphite) with a lateral size of $\sim 1$ nm. The 3DOM W–SiOC material had an overall porosity of $\sim 58\%$, containing textural mesopores and some remaining macropores within the SiOC phase due to incomplete SMP-10 infiltration into certain regions of the 3DOM W scaffold and volume shrinkage of the infiltrated SMP-10 during pyrolysis. The 3DOM W–SiOC material maintained its periodic structure up to 1000 $^\circ$C. At 1300 $^\circ$C, sintering degraded the 3DOM structure. At this high temperature, additional WSi$_x$ and WC$_x$ phases formed, and the free carbon grew in size (from 1.0 nm at 800 $^\circ$C to 2.3 nm) due to continued phase separation. This fabrication method provides an opportunity for preparing different types of interpenetrating nanocomposites and achieving the full functionality of different phases or even obtaining synergistic effects.

Micropillar compression studies of 3DOM W–SiOC show stresses of up to 1.1 GPa achievable at 30 $^\circ$C before brittle failure, a 20-fold increase in stress as compared to the unfilled 3DOM W. Failure was still primarily brittle up to 225 $^\circ$C, whereas high strains and deformability were observed at 425 and 575 $^\circ$C. Considering the energy under the stress–strain curve to be a measure of the energy absorbed during deformation, the maximum
energy absorbed was measured at 425 °C. Compaction banding was observed at 425 and 575 °C, indicating that the material behaves as a low-density solid at these temperatures, which is likely linked to the porosity of the SiOC infiltrant. The high specific strength, as high as 640 MPa/(Mg/m³), along with high deformability at moderate temperatures, make this an ideal candidate material for high temperature applications, as well as future studies into the fundamentals of thermally activated deformation at the nanoscale.
Chapter 7

Summary and Perspectives
7.1 Overall Summary

Nanocomposites have shown superior properties in many aspects compared to their bulk counterparts due to the presence of nanosized features. This dissertation focuses on developing nanocomposites built around metal–organic frameworks (MOFs) and three-dimensionally ordered macroporous (3DOM) materials as potential catalysts and structural materials.

This dissertation has three major parts. A brief summary of the key findings from the work in this dissertation follows. Chapter 2 describes the influence of non-intentional or intentional secondary phases on the mechanical properties of NU-1000 MOF particles. By maintaining phase purity and minimizing defects in NU-1000 crystals, the elastic modulus is enhanced by nearly an order of magnitude, and the introduction of a silica scaffold into part of the mesopore space in the MOF significantly increases the load at failure.

Chapters 3 and 4 present the work of nanocasting MOFs to achieve nanohybrids containing sub-nanosized clusters. As described in Chapter 3, an acid-free silica nanocasting method was developed on the basis of a previously reported silica nanocasting method that employed an acid catalyst. Unlike the original method, the acid-free method can be applied to metastable Ce-MOFs. The product, a silica–oxo cerium cluster nanohybrid material has a remarkably high loading of cerium (51 wt%). Additionally, the Ce species can switch oxidation states between IV and III at 750 °C without aggregation, suggesting its potential as a high-temperature redox catalyst. In Chapter 4, a carbon nanocasting method on NU-1000 was presented. The developed carbon–oxozirconium cluster nanohybrid exhibits a relatively high surface area (266 m²/g), and abundant,
uniformly-sized metal oxo clusters. The electrical conductivity of the current product (0.41 S/m) was only moderate but could possibly be further increased by optimizing the infiltrating precursors.

Chapter 5 and 6 demonstrate the work of investigating the mechanical properties of a 3DOM tungsten (W) material and a 3DOM tungsten–silicon oxycarbide (W–SiOC) material. In Chapter 5, the yield strength of ligaments in 3DOM W was measured by micropillar compression test to be 6.1 GPa, ~6× yield strength of coarse-grained W. In Chapter 6, an interpenetrating 3DOM W–SiOC nanocomposite was developed using 3DOM W as a metallic matrix that was filled with a ceramic phase. The product has well-ordered, and periodic 3D structure. The maximum stress that the 3DOM W–SiOC material could endure was 1.1 GPa at 30 °C, a 20-fold increase compared to the 3DOM W matrix (50 MPa). The deformation mode of 3DOM W–SiOC exhibited a transition from brittle fracture (30 °C, 225 °C) to plastic deformation (425 °C, 575 °C).

The reminder of this chapter discusses the importance and significance of this thesis research and outlines some future perspectives for the current work.

7.2 Outlook for the Investigation on Mechanical Properties of MOFs

Having unique compositional and structural features, MOFs have shown potential in a range of applications. For many applications, it will eventually be necessary to densify and pelletize such MOFs and, therefore, an understanding of the mechanical properties of MOFs is critical. In this dissertation (Chapter 2), nanoindentation using a flat
punch indenter was applied to study the mechanical properties of MOFs. The insights provided in this work, namely, the ability to modulate mechanical properties of NU-1000 particles by controlling non-intentional or intentional secondary phases might also apply to other MOFs, suggesting a potential MOF engineering method to generate more robust MOFs.

This work also provides a simple method to prepare singly dispersed MOF particles for flat punch nanoindentation. Theoretically, any MOF specimen can be prepared in this way, as long as there is a suitable solvent to make the MOF dispersion. In comparison, the commonly used nanoindentation method that employs a Berkovich indenter requires large single crystals or thin-film coatings. Therefore, the development of this method significantly eases the sampling difficulty, greatly extending the scope of MOF species that can be tested.

Additionally, the fact that one MOF particle is processed each time under the indenter has several advantages. Firstly, it provides an opportunity to observe how a single MOF particle responds to pressure in situ. Secondly, the stress state is better tracked and presented during the flat punch indentation compared to when a Berkovich indenter is used, which creates convenience for modeling processes. Lastly, it is possible to measure MOF particles with very small particle sizes using this method because uniaxial compression can be assumed as long as the size of the flat punch indenter tip is larger than the MOF particle.
7.3 Outlook for the Development of MOF-derived Cluster-Containing Nanohybrid Materials

As discussed in Chapter 1, a major purpose of nanocasting MOF materials with silica is to preserve the isolated clusters in MOF materials at rather high temperatures, while the ordered and porous structures are maintained. Higher temperatures can not only expedite the reactions and increase the yield for endothermic reactions, but also suppress coke formation and counteract the activity loss of the catalysts. A pioneering work in this field was done by Malonzo et al. from our group in 2016, who developed a silica–oxozirconium cluster nanohybrid through nanocasting NU-1000. The product was thermally stable up to 500 °C, and preserved the catalytically acidic reactivity of the original clusters.

In Chapter 3, the development of an acid-free nanocasting method extended the silica nanocasting to Ce-MOFs. Considering that different MOFs contain different clusters, which might potentially be catalysts in different reactions, it is meaningful to attempt the acid-free silica nanocasting on other metastable MOF materials. Some promising candidates might be MIL-101 containing Cr₃O clusters, and HKUST-1 containing Cu₂ clusters (Figure 3.1). MIL-101 possesses rather large pores (29–34 Å), which should be suitable for infiltration with appropriate precursors. HKUST-1 possesses smaller pores (10–14 Å), which probably could work as well. Cr₃O and Cu₂ clusters do not have the high symmetry that Zr₆O₈ or Ce₆O₈ clusters have, so they likely tend to aggregate more easily, especially Cu₂ clusters. If nanocasting could be performed on those two MOF materials, the ideal products are silica–CrOₓ cluster nanohybrids, which could potentially be used as...
a catalyst in CO conversion to hydrocarbons (Fischer–Tropsch process), and silica–CuO₅ cluster nanohybrids, which could potentially be used as a catalyst in partial oxidation of methane to methanol.

The silica nanocasting method also opens a new gate for the development of silica-supported catalysts. Compared to other catalyst supports, such as aluminum oxide, zirconium oxide, cerium oxide, etc., silica is a rather inert material. The precursors for catalytically active components usually cannot wet the surface of silica efficiently during catalyst synthesis. In other words, the precursors cannot form strong enough interactions with silica, which makes it difficult to reach the desired degree of loading of the active components. Due to this reason, in the two largest commercial catalytic processes, catalytic reforming and hydroprocessing, the usage of silica as support is less than 1%.

However, thanks to the inert surface, silica also exhibits an advantage over other supports, that it does not get involved into catalytic processes unexpectedly. In contrast, the acid sites in widely used Al₂O₃ supports can catalyze unwanted reactions, such as isomerization or oligomerization.

In the currently developed silica nanocasting approaches, Zr₆O₈ and Ce₆O₈ clusters from the original MOF structures remained stable on the silica supports. These clusters can act as platforms to anchor many other metal species, such as Ni, Zn, Cu, In, Re, Pt, etc., providing the opportunity to fabricate various silica-supported catalysts. Notably, the reason for the stabilization of clusters on silica is still unknown, and it could also be an interesting topic to investigate.
In addition to silica nanocasting, other types of supporting materials for nanocasting are also interesting to investigate, considering the potential synergistic effects they could have with the catalytically active components and the new properties they might introduce. In this dissertation, effort was made regarding this topic and a carbon nanocasting method was developed (Chapter 4), which led to the introduction of electrical conductivity into the developed nanocomposite.

$\text{Al}_2\text{O}_3$ and $\text{TiO}_2$ might also be interesting candidates as the supporting materials for nanocasting. $\text{Al}_2\text{O}_3$ could be considered because it has been used widely as a support in many industrial processes, e.g., CrO$_x$/Al$_2$O$_3$ catalysts for dehydrogenation of light alkanes (Catofin process),$^{136}$ and FeO$_x$/Al$_2$O$_3$ catalyst for ammonia synthesis (Haber-Bosch process),$^{451}$ etc. A relevant work was presented by Zhao et al., who prepared a $\text{Al}_2\text{O}_3$–Cr$_2$O$_3$ nanoparticle hybrid material through mixing aluminum isopropoxide ($\text{Al}(\text{i-OC}_3\text{H}_7)_3$) and MIL-101, followed by heat treatment.$^{452}$ The product had the Cr$_2$O$_3$ nanoparticles (10–20 nm) dispersed on porous Al$_2$O$_3$. It exhibited good selectively (93.2%) and conversion (60.1%) in the reaction of isobutane dehydrogenation. It would be interesting to see if the aluminum precursor could be introduced into the pores of MIL-101 through certain modified methods, thus providing better support for the Cr$_3$O clusters. And if so, further investigation could be performed on how the smaller and maybe evenly-distributed CrO$_x$ species would do differently in the same catalytic reaction.

As for $\text{TiO}_2$, it is well known as an n-type semiconductor photocatalyst,$^{453}$ and its photocatalytic ability could be further enhanced when it is prepared into cocatalyst with certain other metal or metal oxide species.$^{454}$ For example, a $\text{TiO}_2$–NiO nanoparticle hybrid
material exhibited higher photoactivity due to the formation of p-n junction via the introduction of NiO (p-type semiconductor). Another example is a TiO₂–CuO nanoparticle hybrid material that performs better towards the photocatalytic water splitting process because of reduced band gaps. Another relevant work was reported by Jiang et al., who introduced titanium n-butoxide into MIL-101 and then converted it to TiO₂ through dehydration and condensation at 80 °C. However, another work done by Zhao et al. demonstrated that the TiO₂ in the pores of NU-1000 reacted with the oxozirconium clusters and formed ZrₓTi₁₋ₓO₂ at 500 °C. This indicates that the reactivity between TiO₂ and the desired clusters should be considered when TiO₂ nanocasting is attempted.

7.4 Outlook for the Development of 3DOM Materials and 3DOM Material-Based Nanocomposites as Structural Materials

3DOM materials possess many interesting features for mechanical purposes, such as the isotropic, highly ordered and tunable porous structure, and nanosized ligaments. Additionally, the abundant compositional varieties in 3DOM materials make them potentially good candidates in various fields. Therefore, it is meaningful to understand the mechanical properties of 3DOM materials.

The amount of literature focusing on mechanical properties of 3DOM materials is limited to date. Effort was made on investigating the mechanical properties of 3DOM materials with different compositions, including the work in this dissertation (Chapter 5). These works demonstrated that 3DOM materials with certain compositions can
exhibit remarkable strength. A step further on this topic can be studying how different features in 3DOM materials affect their mechanical properties separately. For example, the current work determined the yield strength of 3DOM W ligament to be $\sim 6\times$ of coarse-grained W, and $\sim 2\times$ of 200-nm single crystal W nanopillars.\textsuperscript{241} This overall strengthening effect very likely originated from a combination of various structural features, such as the pore size, the ligament size, the grain size of the ligament, the arch-like architecture of the ligament. Understanding the influence of each individual factor will greatly enrich the knowledge and provide guidance on designing 3DOM materials with desired properties.

Another interesting and promising direction is to make nanocomposites on the basis of 3DOM materials. Having high surface area and interconnected porous structure, 3DOM materials can be processed in various ways. Additionally, they are good candidates for developing isotropic, and interpenetrating nanocomposites. In order for this to be achieved, there are two major pathways, to the best knowledge of the author. The first one is introducing another component into the voids of the 3DOM matrix, like the work demonstrated in Chapter 6. For this direction, one might further consider if a fully dense material or a porous material is desired as the product. In the current work, a preceramic polymeric precursor (SMP-10) was used. Due to the volume shrinkage during the polymer-to-ceramic conversion and incomplete infiltration, the final product (3DOM W–SiOC) had a relatively high degree of porosity. In comparison, introducing small seeds of the precursor into the 3DOM voids followed by nucleation (cycles of seed introduction and nucleation might be needed) can lead to the growth of fully dense phases inside the 3DOM voids.\textsuperscript{410}
The other route is engineering the ligaments of 3DOM materials, aiming to improve the mechanical properties of 3DOM structures while maintaining their porous structures. This can be done by applying a chemical to react with the 3DOM ligaments and partially converting them into another phase,\textsuperscript{373} or coating the original ligaments with another component.\textsuperscript{199} One example is an aluminization technique used by Shetty et al. to partially convert the 3DOM Ni ligaments to Ni\textsubscript{3}Al. The elastic modulus and hardness of the material increased by 17.6\% and 81.6\%, respectively after this process.\textsuperscript{373}
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