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Sol-Gel Processing of Metal-Organic Frameworks

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ABSTRACT: Sol-gel processing represents a powerful and versatile strategy for the preparation of functional inorganic and hybrid materials that facilitate control over the molecular composition, as well as organization of the materials at the various length scales relevant to fundamental and applied research. Recent advances have enabled its use for the processing of an emerging class of functional porous materials called metal-organic frameworks (MOFs). Here, sol-gel approaches can be employed for the direct manipulation of MOFs, or as a route to the construction of composite materials where the properties of the MOF are synergistically combined with those of a carefully chosen inorganic phase. In this review, we present the most significant progress made in this emerging area according to four main synthetic strategies, with a particular focus on describing how sol-gel processing enhances the functionalities of the MOF. These strategies include: (1) molecular scale manipulations of the pore surfaces of MOFs with sol-gel precursors; (2) the controlled positioning or growth of MOF crystals on inorganic surfaces; (3) the use of MOF crystals as templates for sol-gel processes (either within the pores, or at the external surfaces); and (4) the use of sol-gel derived sacrificial inorganic templates for the structuring of MOF-based architectures. Each of these processing methods imparts unique properties to the systems, and provides a route to higher-order architectures and material compositions not accessible through conventional approaches to MOF synthesis. Sol-gel processing provides promising routes toward new functional materials that display enhanced properties, and are expected to play an important role in allowing MOFs to be optimized for specific applications.

1. INTRODUCTION

The design and synthesis of metal-organic frameworks (MOFs) has received considerable attention over the two decades, due in part to their potential use in a wide variety of applications,1-4 including gas storage,5-8 molecular separations,9-12 heterogeneous catalysis,13-17 biotechnology,18-20 biomedical applications,21-25 and integration into functional devices.26-28 The rich chemistry of MOFs has spurred the rapid discovery of a tremendously diverse library of compounds that, in addition to their high surface areas, encompasses a broad range of physical and chemical properties. The versatility associated with MOFs as a materials platform arises as a consequence of the ability to prepare these compounds through a modular synthetic approach, wherein the metal and organic components can be rationally selected combined to induce the formation of the desired framework via a self-assembly process. Although this strategy is powerful in allowing a virtually unlimited number of MOFs to be conveniently prepared, one of the primary needs in the field is the development of advanced processing methods that are compatible with the conditions of self-assembly of the MOF, enabling the materials to be disposed in controlled physical configurations. This is of particular importance.
in high-precision applications such as optics, photonics, electronics, molecular sensing, microfluidics, biotechnology, and energy production, which require the MOF phase to be positioned and oriented with a high degree of control and compatibility with a variety of materials.

In the area of ceramic materials, sol-gel processing has emerged as a pathway to materials that possess highly-controlled molecular and structural organization, which has been demonstrated to enhance their properties and functions. Typically, the term sol-gel is associated with chemical processes that firstly generate a sol, which is a colloidal suspension of submicron-sized particles derived via controlled hydrolysis and condensation of inorganic (e.g. halide or nitrate metal salts) or metal-organic (e.g. metal alkoxides) precursors within a solvent, followed by the formation of a gel upon addition of a catalyst (e.g. a base or an acid). The resulting material consists of a continuous solid backbone that encloses the liquid phase that also adopts the macroscopic shape of the reaction vessel. Further, the solvent phase within the resulting gel can be removed via evaporative or supercritical drying to afford highly porous structures (e.g. xerogels or aerogels) that are not accessible via conventional solid state syntheses.

In addition to the formation of low-density ceramic materials, the versatility of sol-gel processing has led to a considerable body of research dedicated to the processing of other material types (e.g. metals and polymers) and the preparation of hybridized ceramic-based materials that allow other functional systems, such as templating agents, metal or inorganic nanoparticles, and biological materials, to be incorporated within the structures. Importantly, the technique is compatible with many conventional material processing methods (e.g. casting, dip coating, spin coating, doctor blading, and spray coating), allowing the processing of sol-gel derived materials into a variety of structuralized forms, such as nanoparticles, supported thin-films and coatings with controlled thicknesses, patterned surfaces, membranes, and monoliths. In addition, the ability to synthesize solid-state materials from molecular precursors not only provides control over the composition of the materials, but also enables the molecular organization at material interfaces to be precisely manipulated. As a consequence, this has allowed sol-gel processing to emerge as a convenient preparative route for materials used in applications including anticroressive, antireflective and self-cleaning coatings, separation, catalysis, drug release, tissue implants, electronics, optics, energy production, thermal insulation and chemical sensing.

In the context of MOFs, sol-gel processing potentially offers a powerful strategy to boost material performance
through chemical functionalization of the pore surfaces or crystal interfaces, hybridization of the MOF with other material types, the precise spatial positioning and orientation of the MOF crystals, and assembly of the MOF crystals into the desired meso- and macroscopic forms. In this review, we provide an account of the main developments in the application of sol-gel techniques to MOFs, which can be broadly categorized into the four main strategies below. The classifications have been chosen due to the fact that each of the processes act on the MOF phase in a unique manner and at contrasting length scales (Figure 1). Note that the ability to manipulate MOF systems across all length scales (from the molecular scale to the macroscopic scale) is crucial because it enables the precise material properties to be imparted for specific applications. The categories discussed in the following sections are:

1. Chemical functionalization of MOF pores (Section 2; Figure 1, upper left). This is achieved predominantly by post-synthetic modification of a pre-formed framework, wherein chemical reactions are used to directly manipulate certain reactive sites within the pores in order to provide new chemical functionalities. For example, sol-gel precursors (such as organosilicon compounds) can be employed to selectively functionalize framework scaffolds containing metal oxo- or hydroxyl-based backbones.

2. Hybridization of MOFs with ceramics (Section 3; Figure 1, upper right). This approach allows the fabrication of composite materials with synergistic material properties and functions stemming from both components. Here, MOFs are able to act as hosts or templates for post-synthetic sol-gel processing. For example, the pores within the MOF crystals can be used as a compartmentalized space for encapsulation of ceramic nanoparticles, affording MOF/ceramic nanocomposites. Alternatively, the process can be restricted to the external surface of the MOF crystals, giving rise to the formation of core-shell type composites.

In addition to these strategies that post-synthetically modify or hybridize pre-formed MOF crystals, the following two approaches take advantage of the unique ability of sol-gel processing to be carried out in a spatially confined manner, which in turn allows the physical organization of the resulting MOF system to be controlled across various length scales.

3. Positioning of MOF crystallization (Section 4; Figure 1, lower left). The precise control over the positioning of MOFs on target substrates is paramount for their integration within functional devices. The grafting of certain chemical moieties on the surfaces of inorganic materials can provide sites at which MOF crystallization can selectively occur. This leads to the fabrication of MOF-based composites in which the spatial configuration of the MOF phase is highly regulated.

4. Structuring of MOFs at the meso- and macroscales (Section 5; Figure 1, lower right). In this approach, sol-gel processing is used to create higher-order structures (e.g. thin-films or monoliths) of MOFs, whose properties can be considerably enhanced compared to the bulk (powder) form of the material. Here, several new preparative techniques have emerged, including the direct conversion of sol-gel derived ceramic templates into MOFs via treatment with organic ligands.

In the following sections, we discuss each of these four strategies, with a focus on highlighting the influence that sol-gel processing imparts on the properties of the MOF. Illustrative examples from the recent literature are described, and we discuss the advantages and current limitations of each approach. Finally, we describe the future developments in the area that are required to further strengthen the utility of sol-gel techniques for generating MOF-based systems with even greater functionality.

## 2. CHEMICAL FUNCTIONALIZATION OF MOF PORES

The fine-tuning of the properties of MOFs through chemical functionalization of their pores is paramount for applications where the material performance is closely tied to the nature of the host-guest interactions. Although it is possible to introduce certain chemical features at the time of framework construction by using functionalized building blocks, the presence of reactive moieties (e.g. metal complexes and organic functional groups) can often impede the formation of the desired framework structure. In contrast, post-synthetic modifications and infiltrations are often more versatile due to the ability to carry
out a broad scope of well-defined chemical transformations at specific sites within the pores, with preservation of the original scaffold. The insertion of sol-gel precursors, such as organosilicon compounds, can significantly modify the properties of the pores (both in terms of the pore dimensions and the chemical reactivity), and can also provide highly reactive sites that are amenable to further functionalization.

In an early example, the Al(OH)(bdc) framework (Figure 2; MIL-53(Al)) was post-synthetically functionalized with the organosilicon reagent 1,1-ferrocenediyldimethylsilane. Here, the MOF was infiltrated with 1,1-ferrocenediyldimethylsilane under a reduced pressure, and chemical grafting to produce the functionalized compound was achieved by a mild thermal treatment at 65 °C for 72 h. Close investigation of the transformation revealed that the oxygen atoms of the hydroxyl groups that bridge adjacent Al ions within the infinite one-dimensional chains acted as anchoring sites via the formation of silicon-oxygen bonds (see Fig. 2, inset). Interestingly, this process was found to proceed without the concomitant release of an acid (proton), and solid state NMR studies demonstrated a H atom transfer from the hydroxyl group to the cyclopentadienyl ring of the ferrocene moiety.

In a similar preparative procedure, the surfaces of the Al(OH)(abdc) (NH$_2$-MIL-53(Al)) framework was functionalized via a reaction with APTES. Here, the MOF crystals were suspended in ethanol, followed by the addition of APTES and water, and the reaction mixture was stirred at room temperature for 48 h. After washing and drying of the material, it was found that the APTES moieties were grafted to the pore surface via the formation of silicon-oxygen bonds via the bridging hydroxyl oxygen atoms in a similar pathway to that described above. The resulting functionalized MOF was subsequently redox-polymerized with the functionalized sulfonic acid, PAMPS. This composite material exhibited high proton conductivity, which was investigated for use as a proton exchange membrane in fuel cells.

In addition to the chemical modification of surface hydroxyl groups, structure types that feature exposed metal cation sites are also candidates for functionalization via sol-gel precursors. In a recent study, Cu$_3$(btc)$_2$ (HKUST-1) was functionalized with O-POSS to enhance the stability of the framework toward water (Figure 3). O-POSS is a hybrid molecule that takes the form of a well-defined cubic octameric silica cage surrounded by eight hydrophobic isooctyl groups. Following desolvation of the Cu$^{2+}$ sites within the HKUST-1 framework, reflux in a solution containing O-POSS for 48 h resulted in its grafting to the metal sites. Note that, due to the molecular size of O-POSS being larger than the pores of the framework, the chemical functionalization was observed to occur solely at the external crystal surfaces. Nevertheless, the resulting functionalized material showed a remarkably high stability towards moisture, and enhanced hydrophobicity toward liquid water as demonstrated by a considerably higher contact angle of water droplets deposited on the processed samples.

Furthermore, the organic linkers that construct the framework can be provided with reactive functional groups that can later be subjected to further functionalization via sol-gel processing. In one example, the free aldehyde groups within the Zn(ica)$_4$ (ZIF-90) compound were chemically functionalized by immersion in an APTES-containing solution in methanol, followed by reflux at 110 °C for 30 min. The resulting condensation reaction afforded propyltriethoxysilyl groups grafted to the pore surface through an imine functionality (Figure 4). Here, the relatively large size of the APTES molecule relative to that of the internal pores confined the reaction to the outer surfaces of the crystals, providing free triethoxysilyl groups available for further processing while allowing the internal porosity of the framework to be preserved. In an interesting application of this system, ZIF-90...
thin-films grown on porous α-alumina disks could be processed in the same fashion as the bulk crystals, allowing a membrane of the modified material to be tested in gas separations (e.g. H₂/CH₄). The post-synthetically modified material provided enhanced separation performance resulting from its reduced pore aperture size, leading to better exclusion of the larger methane molecules, while also providing a reduction in intercrystalline defects. The chemically functionalized films also exhibited high thermal and hydrolytic stability, which are desirable for industrial hydrogen separations. The membranes were also tested for the separation of equimolar CO₂/CH₄ mixtures at different operational temperatures, showing high selectivity and thermal stability under long-term use.⁹⁹

The molecular functionalization approach can also be carried out with respect to materials that are pre-loaded within the MOF pores. In one recent example, Prussian blue (PB) nanoparticle-loaded within the micro- and mesoporous Fe₆OF(H₂O)₆(bdc)₂ (MIL-101(Fe)) framework could be functionalized via a sol-gel processing.¹⁰⁰ The composite material was firstly dispersed in a slightly acidified solution of ethanol and treated with APTES. The amino-functionalized porous crystals showed biocompatibility characteristics and potential application as a colorimetric biosensor.

**3. HYBRIDIZATION OF MOFS WITH CERAMICS**

We next turn our attention toward using the MOF scaffold as a template for the generation of nanostructured ceramic materials using the sol-gel approach. Here, the well-defined internal structures and external crystal morphologies of MOFs can both be exploited in developing new, nanocomposite systems with a high degree of control over the morphology of the final products. The templating modes supported by the MOF can be generally categorized into those that occur within the MOF network, such as the infiltration of sol-gel solutions and formation of nanoparticles in the pores, and those that are confined to the external surfaces of the MOF crystals, including the embedding of nanoparticles and the formation of shell layers. We now discuss the main advances in each of these areas, with a particular focus on the influence of the MOF template on the sol-gel processed phase.

**3.1 Templating by MOF pores.** In an early demonstration, a Cu²⁺-based framework containing one-dimensional pores, Cu₄(pzdc)₂(dpe) (CPL5), was used as a template for the growth of silica nanoparticles (shown schematically in Figure 5A).¹⁰² Initially, TMOS was infiltrated into the MOF nanochannels by immersion of the MOF crystals within liquid TMOS at room temperature for 30 min. Following removal of the excess precursor under a reduced pressure, the adduct was then exposed to an atmosphere of water vapor for 24 h, followed by heating at 60 °C in air to facilitate hydrolysis and condensation of the alkoxysilane. Additional crosslinking was achieved by heating the material under vacuum at 110 °C, yielding silica nanoparticles homogenously distributed throughout the MOF channels, and having a size restricted to the dimensions of the internal pores. Interestingly, a structural analog of this compound containing smaller pores, Cu₄(pzdc)₂(pz), exhibited almost no formation of silica, suggesting that TMOS was not included within the pores at the precursor loading step. A more recent study probing the properties of CPL5 and HKUST-1 following the deposition of silica nanoparticles (Figure 5B,C) under the same conditions revealed an enhanced adsorption for polar adsorbates (e.g. water and 1,4-dioxane) over non-polar molecules (e.g. cyclohexane).¹⁰³ This was ascribed to the high density of silanol (Si-OH) groups on the surface of the silica nanoparticles within the pores, which are expected to have a greater affinity toward polar guest molecules compared to non-polar species. Interestingly, the dimensionality of the framework pores was also demonstrated to have a significant impact on the relative guest uptakes, with the preference for 1,4-dioxane over cyclohexane being more pronounced in the one-dimensional pores of CPL5 compared to the three-dimensional, interconnected pores of HKUST-1. This is likely due to the ability for molecules to percolate more readily in the three-dimensional pores found in the HKUST-1 structure type, while the molecules must necessarily pass through the silica-modified pores in CPL5, which leads to a selective gating behavior.

Similar synthetic methodologies are available for the formation of other inorganic materials within MOFs, and efforts have been directed towards the incorporation of ceramics to provide additional functionality to the material.¹⁰⁴-¹⁰⁷ In a recent example, titania nanoparticles were formed within the pores of a La₃⁺-based framework, La(btb), via loading of titanium isopropoxide followed by subsequent treatment at 250 °C for 24 h under exposure to water vapor.¹⁰⁵ In a similar result to the case of silica impregnation, the presence of surface hydroxyl groups on the titania nanoparticles enhanced the water adsorption.
capacity compared to the parent material. However, in this case, the oxide phase also introduced a photoresponsive property, wherein the water adsorption behavior of the composite could be influenced by UV irradiation. Here, exposure of the material to UV light resulted in a decrease in the density of hydroxyl groups, as well as the emergence of a reduced Ti$^{3+}$ state within the oxide phase. The same framework was later used to template the formation of ceria nanoparticles by sol-gel processing of cerium tetraisopropoxide at 120 °C under a hydrated atmosphere, giving an partially reduced oxide species in the pores.

The formation of magnetic framework composites (MFCs)$^{109,28}$ via the introduction of magnetic particles into the pores of MOFs is also of significant interest for providing enhanced functionality to MOF systems, including the possibility of manipulating the position and alignment of these materials by means of an external magnetic field.$^{9}$ Despite the dominant approach exploiting the nucleation of MOFs on preformed nanoparticles, post-synthetic infiltration has been explored as an alternative synthetic procedure. For example, the infiltration of aqueous solutions of FeCl$_3$ or FeCl$_2$ into the pores of Cr$_3$OF(H$_2$O)$_9$(bdc)$_2$ (MIL-101(Cr)), followed by the addition of ammonia resulted in the formation of Fe$_3$O$_4$ nanoparticles.$^{110}$ The prepared materials showed an enhanced catalytic activity in the solvent-free oxidation of benzyl alcohols compared to pristine both the parent MIL-101(Cr) and pure Fe$_3$O$_4$ nanoparticles. Importantly, the composite materials were able to be collected via magnetic separation, which has significant advantages over conventional techniques such as filtration, centrifugation, and liquid-liquid separations. It is anticipated that such materials will also be investigated further in areas beyond catalysis, including molecular separations and water decontamination.

The synthetic approach described above can also be taken one step further to provide a pathway to purely inorganic materials via post-processing removal of the MOF. In one successful example,$^{111}$ HKUST-1 crystals (Figure 6A) were immersed in titanium isopropoxide at room temperature for 24 h, washed in ethanol, and then hydrothermally treated in a water/ethanol mixture at 200 °C for 20 h to induce the formation of titania throughout the MOF pores (Figure 6B). The HKUST-1 phase was then digested in hydrochloric acid followed by a final etching process in hydrogen peroxide, affording a crystalline titania architecture exhibiting the morphology of the parent MOF crystals (Figure 6C). The titania structure was shown to possess partially-ordered micropores (ca. 1 nm) disposed with a spacing corresponding approximately to the predominant wall separations present in HKUST-1, as well as disordered mesopores. Interestingly, powder X-ray diffraction data revealed that the titania phase adopted the brookite polymorph, which likely is attributable to a stabilizing influence of the MOF pores, as well as the presence of Cu$^{2+}$ ions during its formation.$^{112}$ More recently, this synthetic technique was further adapted for the preparation of microporous silica via hydrothermal treatment of tetraethoxysilane after loading within the HKUST-1 framework.$^{113}$

### 3.2 Templating by external surfaces of MOF crystals

The ability to precisely control the size, morphology, and surface chemistry of MOF crystals is a tremendous advantage in their use as a template for sol-gel processing. In this area, the studies to date have predominantly focused on the preparation of coatings on the exterior of the MOF crystals to generate core-shell type systems, with an aim of providing the MOF core with an external shell that provides new properties complementing those of the pure MOF.

One of the areas in which surface coatings can benefit MOF crystals is in enhancing the mechanical and chemical resistance of MOFs, which often are brittle and susceptible to decomposition upon exposure to air or moisture following activation of the material. In one study, a mesoporous silica shell formed around MOF crystals was shown to significantly enhance the mechanical properties of the material.$^{114}$ Here, as shown in Figure 7A, a mesoporous silica coating was formed on the surface of crystals of Zn(MeIm)$_2$ (ZIF-8) via alkali-catalyzed hydrolysis of TEOS and the addition CTAC as a mesopore templating agent (step (i)). The CTAC is then removed by calcination to give mesopores that penetrate through the silica shell (step (ii); Figure 7B). This step can also be followed by optional regrowth of the ZIF-8 crystals (or epitaxial
while the shell thickness could be varied by the quantity of TEOS added during the sol-gel process. Meanwhile, titania shells could be deposited using a titanium tetraisopropoxide precursor, and an acid-catalyzed hydrolysis process. Further calcination of the composite materials to a temperature of 500 °C resulted in the decomposition of the organic ligand, and the subsequent formation of hollow dodecahedra composed of ZnO/SiO$_2$ or ZnO/TiO$_2$ (ZIF-8), and Co$_3$O$_4$/SiO$_2$ or Co$_3$O$_4$/TiO$_2$ (ZIF-67). The resulting porous composites showed a significant improvement in photocatalytic water oxidation performance for oxygen production compared to their bulk counterparts.

Although the preceding examples have demonstrated the surface of MOF crystals as being amenable to the direct templating of sol-gel processes, the pre-adsorption of a molecular species capable of facilitating growth of shell layers has also emerged as a versatile synthetic method. In a method often used for the growth of a wide range of different colloidal particles (e.g., Au, Ag, boehmite, polystyrene) on silica surfaces,$^{107}$ the treatment of MOF crystal surfaces with PVP has allowed silica shells to be formed on several different MOF systems.$^{118-120}$ Specifically, after coating MOF crystals with PVP, dense silica films were prepared by immersing the materials in a TEOS-based solution using ammonia as a catalyst (Figure 8A). The thickness and aspect ratio of the as-formed silica shell was tuned by varying the substrate and reaction conditions.$^{108}$

In a more recent study, 60 nm-sized particles of a Tb$^{3+}$-based MOF, Tb(DSCP)$_2$$(H$_2$O)$_n$ (NCP-1) constructed using the anticancer agent DSCP were coated with a 7 nm-thick silica shell (Figure 8B-D).$^{119}$ The ceramic shell could be used to control the dissolution of the MOF in an aqueous solution, leading to a more gradual release of the DSCP from the silica-MOF composites. A similar approach was used to coat the outer surface of a Mn$^{2+}$-based MOF, Mn(bdc)(H$_2$O)$_n$, with a silica shell, followed by the covalent attachment of a cyclic arginine-glycine-aspartate (RGD) peptide, and an organic fluorophore. The RGD-functionalization enhanced the delivery of the MOF-silica composites to human colon cancer (HT-29) cells, allowing for target-specific MRI in vitro.$^{120}$

In addition to the approaches above, pre-formed functionalized nanoparticles can also be used to decorate the surfaces of MOF crystals. For example, epoxy-functionalized silica nanoparticles could be bound to the surface of a mixed-ligand analog of MOF-5 (bdc: 75%; abdc: 25%), whose amino groups were available as anchoring positions.$^{109}$ Interestingly, when the framework was embedded with carbon-coated cobalt nanoparticles,$^{122}$ the treatment process could be readily performed in a microfluidics-type device containing regions of immiscible solvents by using an external magnetic field to maneuver the crystals between reaction and washing zones. A similar preparative procedure for the grafting of pre-formed silica nanoparticles has been performed for the generation of HKUST-1-silica composites.$^{123}$ In this case, silica particles were firstly decorated with thiol groups via reaction of 3-(trimethoxysilyl)-1-propanethiol with the
surface silanol groups decorating the nanoparticles. Then, in a second reaction, Au nanoparticles were attached to the silica surface, leading to the formation of MOF composites decorated with both silica and Au nanoparticles.

In addition to the methods described above that rely on the pre-formed external surfaces of MOFs for templating, a number of systems in which both the MOF and inorganic phases of the composite can be prepared simultaneously have also been recently reported. In one successful demonstration, HKUST-1 mesoporous alumina or HKUST-1-silica composites were simultaneously synthesized via microwave irradiation. Here, the MOF precursors were directly introduced into silica (TEOS) or alumina (acidic boehmite-collodion solution) sols in the presence of a triblock copolymer, poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (EO-PO-EO), and the mixture was subjected to microwave treatment. Powder X-ray diffraction revealed the in-situ formation of the mesoporous alumina or silica phase with the simultaneous growth of the MOF.

In a more recent study, a one-step synthesis of a MOF-silica core-shell composite having a single HKUST-1 core has been reported. In this case, the TEOS solution was introduced dropwise into the MOF precursor solution, and the reaction was assisted by ultrasonication. This led to gelation of the TEOS component and the subsequent growth of a mesoporous coating on the surface of the MOF crystals. The use of ultrasound significantly enhanced the rate of the reaction, and also resulted in composite nanoparticles with narrow size distribution in the 200-400 nm range. In both cases, the success of this approach relied on synchronization of the formation of both phases, which is generally achieved by fine-tuning of the reaction conditions.

4. POSITIONING OF MOF CRYSTALLIZATION

The attractive functionality of MOF-based materials has spurred significant efforts directed toward their combination with other types of materials in order to achieve more sophisticated properties. From a fabrication perspective, the successful integration of MOFs into such platforms relies upon the development of synthetic protocols that facilitate the precise positioning of the MOF on the support, which includes optimization of physical parameters such as the film thickness, surface roughness, crystal alignment, crystal size, and the overall mechanical properties. The controlled deposition of MOFs can be achieved through a variety of pathways, including growth of the MOF on the substrate by layer-by-layer MOF deposition or liquid phase epitaxy, or deposition of pre-formed MOF crystals from colloidal solutions or via Langmuir-Blodgett. A host of other processing techniques, such as the seeded growth method, electro-deposition, microwave synthesis, and gel-layer deposition are also available depending on the configuration of the support and the conditions under which the specific MOF is able to be formed. In this context, the molecular nature of sol-gel processing is highly compatible with the preparative strategies mentioned above, and can provide the necessary chemical interactions between the substrate surface and the MOF for precise positioning of the MOF. Furthermore, these techniques are fundamentally distinct (and likely advantageous) compared to those that employ the MOF phase as a host matrix for nanostructured ceramic-based materials as presented in Section 3.

One of the simplest strategies for positioning MOFs involves the growth of the MOF crystals on surfaces decorated with functional groups that are able to act as chemical anchoring sites. Here, sol-gel precursors are ideal candidates for use as anchoring functionalities due to their ability to be readily grafted to a variety of surfaces, and their high degree of functionalization which can provide a range of different surface chemistries to the support. Spatial control of the coverage of these molecules via surface patterning can provide a mechanism to precisely manipulate the location of MOF crystal deposition. Once the anchoring molecules are positioned, the MOF phase can be grown by methods such as the liquid phase epitaxy or the layer-by-layer growth methods, which have been demonstrated as convenient routes to high-quality films having controlled film thicknesses.

In an early example of this approach, alumina and silica substrates were firstly functionalized by immersion in...
a solution containing 10-undecenyltrichlorosilane, followed by oxidation of the vinyl groups into carboxylic acid groups via treatment with an aqueous solution of potassium permanganate and sodium periodate. Phase-pure MOF-5 films could be subsequently grown on the surfaces by immersion of the substrates in a perpendicular fashion (to avoid coating by sedimentation) in a supersaturated solution of zinc cations and \( \text{H}_2\text{bdc} \) at 20 °C for 24 h. The surface coverage of the film was found to be significantly higher for the carboxylate-decorated surfaces than for bare (untreated) substrates (see Figure 9), as well as those coated with trifluoromethyl groups or a thin sapphire layer, suggesting that the surface carboxylate moieties (which mimic the coordination bonds present in the MOF itself) provide an ideal surface for crystal growth. In an extension of the approach, thin-films consisting of other types of MOFs, including HKUST-1 and \( \text{Zn}_2(\text{bdc})_4(\text{dabco}) \), could also be grown in a similar fashion.\(^{146}\) Interestingly, the HKUST-1 films were found to display a preferential growth orientations on carboxylate-functionalized surfaces (111) and c-plane sapphire-coated (100) surfaces, further confirming the unique influence of the surface treatment on the resulting films.

In a related study, functionalized silicon substrates were used as supports for porphyrin-based MOFs grown by the layer-by-layer method (Figure 10).\(^{148}\) Here, the hydroxyl groups at the surface of support acted as nucleophiles toward the sol-gel precursor APTMS, facilitating its immobilization on the surface. The amine functionalities of the molecule remained freely available for the binding of \( \text{Zn}^{2+} \) cations, and subsequently facilitated the formation of MOF by cycling between solutions containing the metal source (step I), a carboxylate linker (L1 or L2) to complete square grid-type layers consisting of dinuclear paddlewheel units (step II), and a bipyridine-based pillar linker (P1 or P2) to allow further layers to be deposited thereon (step III). A consequence of this stepwise formation of the framework is the ability to precisely control of film thickness, which could be calibrated based on the number of growth cycles employed during the fabrication procedure.

Similarly, APTES-functionalized surfaces of titania were also demonstrated to be excellent surfaces for the growth of crystalline ZIF-7, -8, and \( \text{Zn}(\text{aBnIm})_2 \) (ZIF-22) membranes due to the strong coordination between the amine functionalities of the APTES molecule and the \( \text{Zn}^{2+} \) centers that are used in the construction of the framework.\(^{95}\) Similar approaches were subsequently employed for the synthesis of ZIF-90 membranes on porous alumina ceramic supports, where APTES was firstly grafted in a condensation reaction with the hydroxyl groups at the surface of the support, followed by reaction of the amine group of the APTES molecule with the aldehyde groups of the linker via imine condensation. The anchored moieties then facilitated crystal nucleation and growth, resulting in high-quality ZIF-90 films on the porous support. This approach could also be extended to APTES-functionalized fused silica fibers, demonstrating that the use of sol-gel precursors as anchoring agents is not limited to flat surfaces.\(^{149}\) Indeed, amine-modified alumina nanoparticles were also found to be effective for the nucleation of ZIF-8 membranes on coarse mesoporous supports.\(^{150}\) In this case, a high density of nanoparticles on the support was demonstrated to be crucial for the growth of continuous membranes.

In addition to functionalization of metal and ceramic surfaces by sol-gel precursors, the use of functional ceramic nanoparticles derived by sol-gel processing can also be used as selective growth sites for MOF crystals. Here, a particularly powerful method for the fabrication of the substrates is the so-called Söderberg method,\(^{39}\) which is a solution-based method that facilitates the controlled hy-
drolysis of alkyl silicates and results in the formation of highly monodisperse silica particles. Modifications to the original conditions have allowed the chemical functionality of the surfaces of the resulting nanoparticles to be tuned to allow MOFs to be grown on their external surfaces. In one example, silica nanoparticles were firstly synthesized using TEOS and VTES or APTES as precursors and ammonia as catalyst, affording nanoparticles featuring precisely-tuned bulk compositions and vinyl (VTES) or amine (APTES) surface functionalizations. In the case of the vinyl-functionalized material, the vinyl groups were oxidized into carboxylic acid groups, and the addition of the particles into a MOF-5 crystallization solution resulted in the formation of MOF-5 crystals that emerged with a greatly enhanced crystallization rate (up to 10 times faster) compared to conventional solvothermal syntheses. The amine-functionalized nanoparticles also exhibited good seeding performance, although the size dispersion was found to be somewhat greater (17%, compared with 4.8% for the carboxylate functionalized material) after a 10 h reaction at 95 °C. Interestingly, deposition of the functionalized silica nanoparticles on bare silicon wafer substrates allowed MOF-5 films to be formed without substrate modifications prior to film deposition, demonstrating that such seeded growth mechanisms can also be used for the effective coating of MOFs on supports that are conventionally regarded as poor substrates for crystal growth.

Similarly, magnetic iron oxide/silica core-shell nanoparticles decorated with carboxylic acid groups were found to act as effective nucleation agents for the growth of HKUST-1 crystals. In this case, the Stöber approach was adapted wherein commercially available iron oxide/silica nanoparticles (see Figure 11A-B) were firstly treated with APTES (and an ammonia catalyst), resulting in chemical grafting to the surface via hydrolysis and a subsequent condensation reaction. The amine-functionalized nanoparticles were collected by way of a magnet, treated with a glutaraldehyde solution to install surface aldehyde groups, and the aldehyde was further oxidized to a carboxylate moiety in a potassium permanganate solution. Then, the liquid phase epitaxy method was employed to grow HKUST-1 by immersing the particles into solutions containing metal ions and linker molecules in an alternating fashion. The resulting composite maintained the magnetic core of the parent nanoparticles, and the thickness of the MOF layer could be conveniently adjusted by programming the appropriate number of deposition cycles (see Figure 11C-D). A very similar approach could also be used for fused silica surfaces modified with COOH-terminated SAMs for the growth of MOF-5 membranes grown in a layer-by-layer fashion.

In a more recent example, the Stöber method has been used to generate particles featuring more complex architectures, namely silica-on-silica (SOS) spheres. Here, CTAB, MPTMS, ammonia, and polyvinyl alcohol were combined in a one-pot fashion in a water/methanol solution, resulting in the initial formation of silica microspheres followed by the nucleation and growth of secondary silica nanospheres on the microsphere surface. Subsequently, the surface of the SOS was modified with carboxylate groups (via a maleimide-thiol coupling) or amine groups (through the addition of APTES). Following treatment of the SOS particles in an alcohol-based solution containing Cu²⁺ cations to induce impregnation of metal ions into the material, the H₃btc linker was added to induce preferential growth of the HKUST-1 crystals on the microspheres. Similarly, carboxylic acid-functionalized silica nanoparticles facilitated the selective growth of ZIF-8 via the initial loading of Zn²⁺ cations followed by the addition of HMIm to induce formation of the framework phase on the particle surface. The resulting product could be isolated and treated to subsequent growth cycles to increase the thickness of the resulting ZIF layer (see Figure 12A-D). After three growth cycles, the particle size of the nanoparticles had grown from 3.0 to 3.8 µm, indicating an approximate film thickness of 400 nm. The coated particles could be loaded as the stationary phase in high-performance liquid chromatography, which demonstrated a promising separation performance for relatively large molecules such as endocrine-disrupting chemicals (e.g. bisphenol A, β-estradiol, and p-(tert-octyl)phenol) and pesticides (e.g. thiamethoxam, hexaflumuron, chlorantraniliprole, and pymetrozine).

In addition to the growth of MOFs on preformed sol-gel derived supports, the ceramic phase can also be generated in-situ during MOF formation via a surfactant-assisted pathway. For example, the addition of the Pluronic F-127 surfactant into the MOF-5 precursor solution resulted in...
the formation of zinc phosphate (α-hopeite) spherical microparticles, whose phosphate component originates from the considerable quantities of phosphorous found within commercial batches of the surfactant.119 The ceramic particles were then found to be excellent seeds for the nucleation and growth of MOF-5, leading to a 3-fold increase in the rate of MOF growth. The ability to spatially position the MOF growth was further demonstrated by the positioning of isolated α-hopeite particles on microfabricated wells, followed by a MOF synthesis step. This method was also shown to be sufficiently versatile to allow metal nanoparticles (e.g. platinum and palladium) to be first incorporated within the ceramic particles as a functional component, followed by their incorporation into MOF-5 via addition of the material into a N,N-diethylformamide-based MOF-5 growth solution. More recently, zinc oxide ceramic particles were shown to serve as effective nucleation agents for the rapid growth of a range of Zn-based MOFs including MOF-5, Zn4O(abdc)3 (IRMOF-3), Zn4O(2,6-ndc)3 (IRMOF-8), and Zn4O(bpdc)3 (IRMOF-10).160 In-situ synchrotron SAXS investigation revealed MOF crystal growth occurred within minutes following the injection of the ZnO particles (Figure 12E). This phenomenon was found to occur for a variety of particle sizes, including nanometer-sized particles. An advantage using smaller particles in this technique over larger microparticles is the relatively small influence of the dense ceramic phase on the surface area and sorption capacities, and the compatibility of the material with microcontact printing technologies. This is of promise for the fabrication of MOF-based devices, which was demonstrated by the use of a microfluidic system to initially position zinc oxide particles inside the channel, followed by conversion to the corresponding MOF patterns at room temperature. Note that the ability to convert the nanoparticles at room temperature is unique to this heterogeneous seeding protocol, which potentially offers a facile method for the fabrication of functional MOF-based devices.

The top-down patterning of sol-gel derived thin-films has also been investigated as a method of spatially positioning MOF crystals. In an initial report,161 Co(BnIm)2(ZIF-9) powders were firstly deposited on a PhTES-based thin-film, resulting in a uniform coverage of the crystals on the material surface (see Figure 13). Here, the PhTES film plays a crucial role because the film softens under heating, allowing for a slight sintering of the ZIF-9 particles. Then, the film was subsequently exposed to hard X-rays at a lithographic synchrotron facility, allowing regions of the not exposed to the radiation to be etched with ethanol to allow the top-down formation MOF patterns via use of a suitably designed mask. In another example, an approach that involves the immobilization of
insoluble Cu-based precursors (mainly a mixture of Cu$_2$(OH)$_3$(NO$_3$) and Cu(NH$_3$)$_4$(NO$_3$)$_2$) on a sol-gel film based on APTMS with GPTMS was reported.$^{163}$ The precursors could be converted to HKUST-1 in a similar manner to bulk copper hydroxide,$^{164}$ allowing the growth of HKUST-1 films or patterns via exposure to an alcoholic solution containing H$_2$btc.$^{165}$

5. STRUCTURING OF MOFS AT MESO- AND MACROScales

Interfacial processes that convert one solid-state material into another under changing chemical and physical environments are ubiquitous in nature, particularly in transformations such as chemical weathering.$^{166,167}$ Such transformations are facilitated through the formation of a thin solid-fluid interface that promotes dissolution of the original material, followed by the immediate recrystallization of the product phase.$^{168,169}$ This phenomenon, often referred to as pseudomorphic transformation, leads to material conversion with retention of the shape and dimensions of the original feedstock material, provided that the product phase nucleates and grows more rapidly than the speed of dissolution of the parent phase. Although conversions of this type have been known for some time for inorganic minerals on the geological timescale, they have only recently begun to be recognized as a potentially powerful tool for the fabrication of functional materials.

In this context, sol-gel processing has a crucial role to play in providing researchers with a diverse platform of template materials that are well-controlled both in terms of composition and structure. Early demonstrations of this approach involving the preparation of ordered mesoporous silica$^{170}$ and three-dimensionally ordered arrays of zeolite nanocrystals$^{171}$ from structuralized oxide precursors have stimulated a growing interest toward the fabrication of higher-order architectures of MOF-based materials. In this section, we present a discussion on the application of sol-gel (and some related) processing methods for the preparation of sacrificial inorganic templates for MOF growth. In particular, we focus on illustrating the versatility of the synthetic approach, and highlight the unique influence the structuration can have in determining the overall properties of the MOF-based systems.

In an initial application of this approach, sol-gel derived mesoscopic alumina templates were converted to MOF architectures possessing controlled textural properties both at the micro- and macroscale.$^{172}$ Here, hierarchically porous, amorphous alumina aerogels containing mesopores were prepared from a mixed water/ethanol solution containing AlCl$_3$$\cdot$6H$_2$O with the addition of propylene oxide as a gelation agent, followed by supercritical drying.$^{173}$ Meanwhile, aerogels further possessing macropores could be obtained by a similar route using phase separation via dissolution of poly(ethylene oxide) within the reaction mixture at the time of gelation. These structures could be converted by the reaction with appropriate organic linkers under hydrothermal conditions using microwave irradiation into mesoscopic architectures of several different Al-based frameworks, including Al(OH)(1,4-ndc) (macroporous aerogel depicted in Figure 14A), MIL-53(Al) and [Al$_5$O(OH)(H$_2$O)$_3$](btc)$_2$ (MIL-100(Al)). The versatility of the synthetic approach was further demonstrated through the replication of three-dimensional inverse opal structures (Figure 14B) and two-dimensional patterns, which could also be converted under similar reaction conditions. In the case of the aerogel architectures of Al(OH)(1,4-ndc), the benefits of structuration were demonstrated via an increased efficiency in liquid-phase water-ethanol separations, wherein the macroporous replicate displayed a significantly enhanced separation performance compared to both the mesoporous aerogel and powder forms of the MOF. The superior properties were attributed to the greater diffusion rates through the macropores of the Al(OH)(1,4-ndc) aerogel architecture.

A similar synthetic approach was later used for the replication of alumina-based nanofibers prepared by the...
The pseudomorphic transformation strategy has also been explored for other ceramic materials. For example, zinc oxide flakes and patterned films created by means of electrospinning method from a mixture of Al(NO$_3$)$_3$·9H$_2$O and PMGI.$^{174}$ Large-scale freestanding mats composed of MOF/alumina composite fibers (Figure 14C) were obtained by partially transforming the amorphous alumina fibers in the presence of aqueous solution of either H$_2$(1,4-ndc) or H$_2$bdc under microwave irradiation. The resulting composite fibers demonstrated sorption properties characteristic of hierarchically porous materials, combining the macroporosity originating from the voids existing between the nanofibers with the mesoporosity stemming from the unconverted amorphous alumina phase and the micropores of the MOF crystals.

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Although the coordination replication technique has largely been investigated using oxide-based precursors, a number of recent studies have also demonstrated that other inorganic materials also display suitable reactivities for use as templates. For example, films, patterns, and three-dimensional structures composed of homogeneously intergrown crystals of HKUST-1 were prepared from copper hydroxide nanotubes formed through the surface oxidation of copper metal using sodium persulfate.$^{178}$ A variety of substrates could be used for the conversion, including a copper mesh, a copper grid and a printed electronic circuit board, evidencing the versatility of the method. In another study,$^{179}$ mechanically stable monolithic architectures of HKUST-1 were also obtained by the conversion of an amorphous, macroporous copper hydroxide-PAAm composite phase prepared by phase separation.$^{180}$ In this case, the polymer phase represented a vital structural component in order to provide both the starting copper hydroxide colloidal matrix and the replicated HKUST-1 monolith with mechanical rigidity. The mechanical properties of the monolith were not greatly diminished following the conversion process, as demonstrated by the stress at catastrophic failure of the parent material (2.5 MPa) and the final product (1.5 MPa). More recently, a copper hydroxide-PAAm composite has been used for conversion to two- and three-dimensional flexible MOFs, Cu(bdc)$_2$(MeOH)$_3$ and Cu(bdc)$_2$(py), respectively.$^{181}$ Here, the structuralization was shown to have an considerable impact on both the adsorptive and dynamic properties of Cu(bdc)$_2$(MeOH)$_3$, which arises due to the immobilization and anchoring of the crystals to the PAAm backbone.

In a further demonstration, the coordination replication strategy was used for the direct conversion of bio-mineralized forms of calcium carbonate into superstructures of calcium-based MOFs.$^{182}$ These bio-minerals are invariably generated by organisms to provide specific functions (such as robust skeletal components), and many display highly organized, hierarchical structures that are difficult to duplicate using laboratory approaches. In this work, a variety of samples, including marine corals and tests (shells), could be immersed in aqueous solutions of H$_2$sq or H$_2$dhbq and converted into architectures.
of the Ca(sq)(H₂O) and Ca(dhbq)(H₂O)₂ frameworks, respectively. The ability to readily prepare the MOF architectures from such naturally-sourced inorganic materials is promising for combining the attractive features of the MOFs with the functionalities of the parent phase that stem from the unique structures of the materials.

The ability of inorganic materials to be processed into two-dimensional films has also encouraged their investigation in the formation of MOF-based membranes in applications such as gas separations. For example, free-standing membranes consisting of HKUST-1 were achieved on a centimeter scale at room temperature by using free standing copper hydroxide nanostand (CHN) films as a sacrificial substrate, while zinc hydroxide nanostrands could be used for the preparation of ZIF-8 membranes. Recently, ZIF-8 films were successfully integrated with quartz crystal microbalance (QCM) substrates via conversion of zinc oxide layers deposited by atomic layer deposition (ALD), enabling molecular adsorption within ZIF-8 to be monitored by the QCM technique. In the same work, alumina films produced by ALD were also shown to be readily replicated to the Al(OH)(1,4-ndc) framework, demonstrating the versatility of the technique.

While most of the studies discussed above have focused on the full conversion of a sacrificial template to the MOF phase during the conversion process, the pseudomorphic replication strategy is amenable to the preparation of heterostructured MOF-inorganic composites, either by partial conversion of the sacrificial template, or the use of a preorganized composite template in which only one of the phases undergoes conversion to the MOF. This promise of this approach lies in the potential integration of complementary material properties, providing materials with greater functionality. An elegant example of such a strategy was recently demonstrated using alumina-coated gold nanorods, where the alumina phase was selectively converted into a Al(OH)(1,4-ndc) shell layer, leaving the gold cores intact following the replication process. Here, the photothermal conversion ability of the gold nanorods acts as an optical switch that enables the guest molecules adsorbed within the MOF pores to be spatially and temporally released through under irradiation of near-infrared light via a local heating mechanism.

A similar approach toward generating core-shell systems was carried out for the conversion of Cu₃O shells deposited on the surface of various types of noble metal nanoparticles (Au nanoparticles, Pd nanocubes and Pt-on-Au dendritic nanoparticles), generating HKUST-1-nanocrystal assemblies (Figure 15). Here, the mildly acidic conditions imposed by the solution of the partially-dissolved H₂btc linker promotes the oxidative dissolution of the Cu₃O shell, from which the copper cations are liberated for the construction of the MOF framework. As a result, well-defined yolk-shell structures were obtained and probed as size selective heterogeneous catalysts for the liquid-phase hydrogenation of olefins.

In an example of the controlled partial conversion of a functional parent phase, core-shell heterostructures of a semiconductor-MOF composite were prepared via the replication of the surface of zinc oxide rods to a polycrystalline ZIF-8 shell (Figure 16). In this work, zinc oxide nanotube arrays were first grown on a FTO-coated glass by means of galvanostatic electrodeposition, followed by subsequent partial dissolution. The zinc oxide nanotube arrays were then partially converted into ZIF-8 under solvothermal treatment in the presence of HMeIM dissolved within a DMF/H₂O mixture. The combination of the photoelectric properties of zinc oxide with the size selectivity displayed by the MOF shell was exploited to create a novel type of photoelectrochemical sensor. This new device was used for selectively sensing two reductive species of different size, namely hydrogen peroxide and ascorbic acid. Here, the ability for the system to discriminate between the two molecules is provided by the ZIF-8 coating, whose pores permit the diffusion of hydrogen peroxide, but not ascorbic acid. Once the hydrogen peroxide reaches the zinc oxide surface, it triggers a great enhancement in the photocurrent response, which can be externally observed (Figure 16D).

In a final example involving the assembly of a heterostructured system, crystals of the Al(OH)(ipa) (CAU-10-H) were grown by replication of the oxide layer naturally existing on metal aluminum surfaces. In this case, the CAU-10-H system displays an s-shaped water adsorption isotherm at 298 K with a pronounced water adsorption step at P/P° ≤ 0.35, which renders it advantageous for applications in water adsorption-driven heat pumps and chillers. Because the metallic aluminum support is a good heat conductor, the deposition of the CAU-10-H crystals directly on its surface enables optimization of the performance of the adsorbent at the device level by improving its thermal conductivity.
26. CONCLUSIONS AND OUTLOOK

As described in the foregoing sections, sol-gel techniques offer a versatile set of pathways for the functionalization of MOFs and their processing into configurations that exhibit unprecedented functional properties. In this context, the well-developed chemistry of inorganic materials provides a strong foundation for the integration of MOFs into nanostructured, sol-gel derived ceramic materials, and significant advances are being made with respect to the development of processing strategies for pure MOF systems. Such progress is expected to be crucial in providing MOFs with the precise properties required for specific applications, or for boosting the performance of existing devices where the high level of permanent porosity, selective adsorption, and structural response to certain guest molecules can be harnessed to install new functionalities to the systems. However, significant synthetic challenges still remain in the area, and further studies devoted to expanding the scope of MOFs that can be processed, as well as enhancing the structuralization precision across all length scales (from the molecular scale to the macroscale) are expected to be of paramount importance if MOFs are to be used in real-world applications. Fundamental to such advances will be a deeper understanding of how the sol-gel processing parameters, including the identity of the precursors, catalyst and solvents, and the reaction conditions (such as the temperature, concentration, and reaction time) influence the composition, structure and properties of the resulting systems.

In the area of post-synthetically functionalizing the interior surfaces of MOFs with sol-gel precursors, the ability to direct the resulting pore chemistry via rational selection from an extensive library of organosilicate and related molecules is of promise in fine-tuning the properties of the MOF. A particular advantage of this technique is that the framework can be rationally selected on the basis of its structural and chemical properties, allowing the best possible combination with the sol-gel precursor. However, further studies directed toward ascertaining the influence of installing such highly reactive or polar groups within the pores via this method on the adsorption properties would assist in clarifying the potential utility of this processing strategy for applications such as molecular separations. A more detailed knowledge of the reactivity of the functional groups following grafting to the surface would also reveal the possibility for further molecular-scale manipulations to optimize the pore environments for adsorption-based applications or chemical conversions.

Meanwhile, the hybridization of MOFs with ceramic materials has provided potential pathways to synergistically combine the properties of MOFs with those of nanostructured inorganic materials. In the case of ceramic nanoparticles grown in the channels of the MOF, the size can be limited to within a narrow range constrained by the dimensions of the pores. Alternatively, the unique chemical environment of MOF pores and crystal surfaces can be utilized for the templating of inorganic materials with unique structures. The development of new composite materials that takes advantage of the interactions between the MOF and ceramic phases may give rise to rich phenomena relevant to optics, photonics and electronics applications. Fabrication methods that allow the porosity of the MOF to be preserved following growth of the inorganic material may also provide new adsorption phenomena stemming from the presence of the two phases.

A significant body of research related to the positioning of MOFs using sol-gel precursors, and growth and anchoring of MOF crystals on sol-gel derived ceramic materials has also recently emerged. An attractive feature of these approaches is the versatility of the synthetic protocols, and the extension of the synthetic protocols to allow the immobilization of a greater scope of functional MOFs (such as those possessing exposed metal cation sites or reactive functional groups) could provide materials suitable for coatings or membranes in a host of industrially-relevant applications. Further, the development of systems that synergistically combine the attractive properties of both the MOF and the support would be an important endeavor in the fabrication of next-generation materials with enhanced properties in applications such as electronics and molecular sensing.

The conversion of sacrificial sol-gel derived inorganic templates into structuralized forms of MOFs is a recent development that may greatly assist in the immobilization.
tion of MOF crystals in higher-order systems. The ability to employ the well-established protocols for preparing sol-gel derived ceramics, which for many specific systems allow the molecular composition, porosity, and macroscopic shaping to be well-controlled in a convenient, one-pot preparative strategy is expected to allow the generation of a greater variety of ceramic templates (both in composition and in structure) suitable for conversion into MOFs. Furthermore, systematic studies targeted toward elucidating the influence of the structuralization by comparing their adsorptive and dynamic properties to those of bulk (crystalline powder) forms would allow their performance to be better characterized in physical configurations close those required for deployment in real-world systems.

The research areas described here represent the main emerging areas in which sol-gel techniques have been applied in MOF chemistry to date. Future studies are not only expected to build upon these early examples, but to also introduce new processing elements that will provide further enhancements to the properties of MOFs. The unique contributions from researchers possessing expertise in traditional sol-gel science are expected to accelerate progress in this area, and the resulting materials are likely to provide new, rich interfaces between MOF chemistry and other areas of science and technology, including electronics and biotechnology.

ASSOCIATED CONTENT
Supporting Information

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ABBREVIATIONS
abdc\(^-\) 2-amino-1,4-benzenedicarboxylate
ALD atomic layer deposition


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