Metal–Organic Frameworks

DOI: 10.1002/anie.201001684

Oriented Nanoscale Films of Metal–Organic Frameworks By Room-Temperature Gel-Layer Synthesis**

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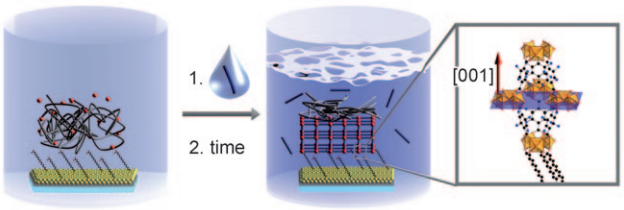
Metal–organic frameworks (MOFs) assembled from organic building blocks and metal-based connectors have attracted much interest owing to their large pores and their enormous structural diversity. Particularly, the generation of homogeneous thin films of MOFs is highly desirable in view of potential applications including chemical sensors, catalysts, and also optical devices. Several elegant examples of MOF film growth have recently been reported (see below), but a general and convenient method for the synthesis of homogeneous oriented thin films is not known. Herein we present a novel strategy for the growth of highly oriented thin films of MOFs based on the storage of one reaction partner for framework synthesis in a polymer gel layer, followed by diffusion of the other reaction partner into the gel layer and to a nucleation interface provided by a functionalized self-assembled monolayer (Scheme 1).



Scheme 1. Representation of the gel-layer approach leading to uniquely oriented nanoscale films of metal–organic frameworks. A SAM-functionalized gold slide is loaded with the metal-salt-containing poly(ethylene glycol) gel layer (metal ions in red) and covered with a solution containing the linker molecules (blue).

The unique structural and chemical features of metal-organic frameworks (MOFs)[1] make them attractive hosts for gas storage,[2] gas purification,[3] catalysis,[4] separation,[5] and chemical sensing.[6] MOFs consist of molecular linkers and vertices that are typically occupied by molecular complexes or cluster entities (secondary building units; SBUs).[7] MOFs can be either rigid or flexible, depending on the linker component, the free space within the structure, and on different host–guest interactions. The extreme sensitivity and selectivity of flexible MOFs towards guest molecules is a promising feature regarding possible applications such as chemical sensors.[8] For chemical sensing, membrane separations, optical devices, and for the assembly of complex nanoscale structures, it would be highly desirable to obtain thin oriented MOF films. Two different methods for the synthesis of MOF thin films have been recently developed: direct growth from solvothermally pretreated solutions,[9–11] and step-by-step growth from molecular precursors.[12]

Thin-film synthesis of MOFs from solvothermally pretreated solutions was recently realized in the cases of $[Zn_4O(BDC)_3]$ (BDC^{2-} = 1,4-benzenedicarboxylate; MOF-5),[9] $[Cu_3(BTC)_2]$ (BTC^{3-} = 1,3,5-benzenetricarboxylate; HKUST-1),[10] and flexible $[Fe_3O(BDC)_3(OAc)]$ (Fe-MIL-88B).[11] Depending on the synthetic procedure, the films have more-or-less densely packed oriented crystals or islands of crystals. An alternative step-by-step growth concept based on alternating exposure to the molecular linkers and metal ions was also developed, thus generating very thin and homogeneous layers of HKUST-1.[10] To the best of our knowledge, the step-by-step approach has only been applied to rigid MOF structures containing an $[M_2(CO_2)_4]$ ($M = Zn^{2+}$, Cu^{2+}) paddlewheel motif as the SBU.

Based on the insights obtained from the recent work on MOF film synthesis, we aimed at developing an alternative, more general approach that would allow us to supply the reactants at high concentrations into a thin layer close to the nucleating surface of the functionalized self-assembled monolayers. As we show below, this was achieved by storing one reaction partner for framework synthesis in a polymer gel layer, followed by diffusion of the other reaction partner into the gel layer and to a nucleation interface provided by a functionalized self-assembled monolayer.

Organogels have been used in bulk MOF synthesis to obtain well-shaped single crystals for crystallography.[13,14] For this purpose, metal ions are embedded in poly(ethylene oxide) gels and kept separated from the linker solution. Slow diffusion of the organic linker into the metal-ion-charged gel creates few nucleation centers and allows for the growth of large crystals. The advantage of the poly(ethylene oxide) gels is their compatibility with both aqueous and non-aqueous media. The water content strongly affects the behavior of the gel owing to the formation of hydrogen bonds.[15] Importantly, in contrast to the above "classical" gel synthesis, we use a thin gel layer as a storage medium for complexed metal ions at high concentrations near the nucleating surface of a function-

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[**] Financial assistance from DFG (SPP 1362) is gratefully acknowledged. The authors would like to thank Dr. S. Schmidt and B. Rühle for the help in sample characterization.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201001684.

alized SAM to achieve a high heterogeneous nucleation rate for film growth (Scheme 1).

Based on our previous work on HKUST-1 films,[10] this structure was selected to develop the new gel approach for MOF film synthesis that was subsequently adapted to the amino-functionalized, flexible framework $[Fe_3O(NH_2\text{-}BDC)_3Cl]$ ($NH_2\text{-}BDC^{2-}$ = 2-amino-1,4-benzenedicarboxylate; Fe-MIL-88B_NH_2).[16] The oriented growth of amino-functionalized MILs was also recently studied by our group and will be reported elsewhere. Both MOF structures have fundamentally different topologies, SBU motifs, and flexibilities, and also different conditions for bulk synthesis. They serve as representative examples for the high adaptability of the newly developed approach (see the Supporting Information for detailed synthetic conditions and structural descriptions of both MOFs).

The newly developed gel layer approach does not require an elaborate preconditioning of the growth solutions or a multiple alternating immersion of the functionalized surface in solutions of the reactants. First, the required SAM-coated gold substrates were prepared using 16-mercapto-hexadecanoic acid (16-MHDA) or 16-mercaptohexadecanol (16-MHD) according to literature procedures[17] (Supporting Information). After synthesis, we observed growth of both porous frameworks on each SAM-modified surface, but not on bare gold surfaces.

The growth of HKUST-1 films on the functionalized surfaces was confirmed by the comparison of X-ray diffraction data with those from the bulk material (Figure 1). In all

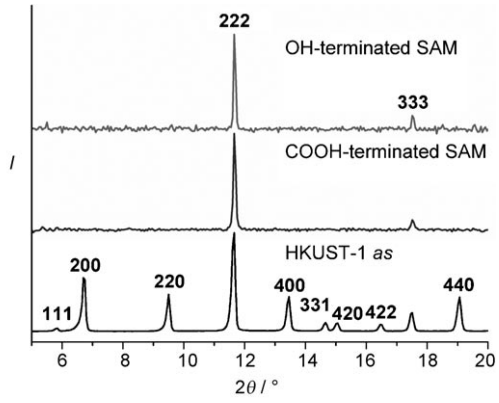

Figure 1. X-ray diffraction data (background-corrected) of HKUST-1 thin films on COOH- and OH-functionalized gold surfaces in comparison to a powder sample. Each pattern is normalized to the most-intense reflection.

the samples, highly preferred orientation in the (111) direction is indicated, and is independent of the termination of the SAM. The results are in good agreement with those from earlier investigations on the Cu-HKUST-1 system.[10] Scanning electron micrographs of HKUST-1 grown on OH-functionalized SAMs are presented in Figure 3a.

The main focus of this work was on oriented nanoscale films of the flexible porous framework Fe-MIL-88B_NH_2. Following the synthetic procedure for gel layers, Fe-MIL-88B_NH_2 films were obtained after 96 h immersion time at room temperature and characterized by X-ray diffraction (Figure 2). In the case of OH-functionalized SAMs, crystal

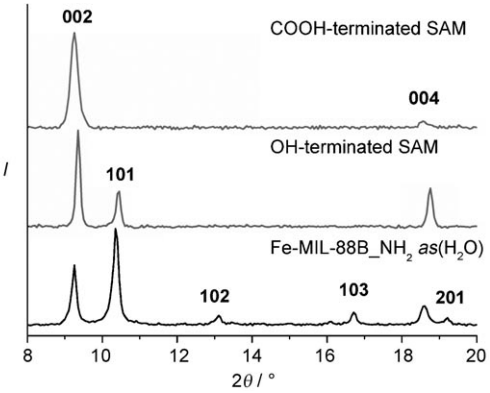

Figure 2. X-ray diffraction data (background-corrected) of Fe-MIL-88B_NH_2 on each functionalized surface, after 96 h immersion time, in comparison to the H_2O-exchanged form of the powder sample. For COOH-functionalized SAMs, a unique [001] orientation is observed.

orientations along [001] and [101] are observed. In contrast, with a COOH-functionalized SAM, only the unique [001] orientation of the MIL-88B framework was observed.

The greater width of the (002) reflection indicates the formation of a thin layer composed of small crystals/domains, which was confirmed by SEM micrographs (Figure 3b). It can be clearly seen that a very homogenous and oriented layer can be obtained, with crystal sizes of about 40 nm. The thickness of this film was also about 40 nm (cross-section SEM) and its root-mean-square surface roughness was 5–9 nm (from atomic force microscope images; see Supporting Information).

The (001) orientation is the same as the that observed during the crystallization of the precursors for Fe-MIL-88B

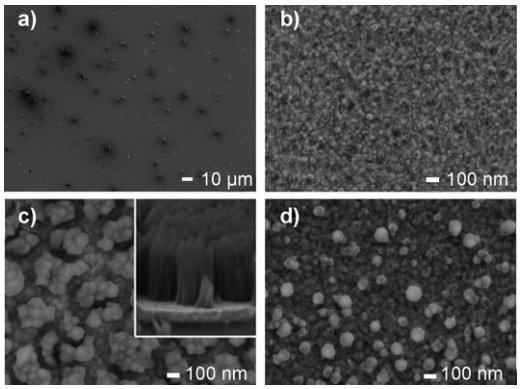

Figure 3. Scanning electron micrographs of HKUST-1 on an OH-functionalized substrate (a), and of nanoscale, homogeneous films of Fe-MIL-88B_NH_2 on COOH-functionalized substrates (b). The use of higher iron(III) concentrations led to thicker films of Fe-MIL-88B_NH_2 with the observed island formation (c); the thickness was estimated to be 500–550 nm from a cross-section SEM (inset). With the application of higher-molecular-weight PEO (100000), larger single crystals of Fe-MIL-88B_NH_2 on the surface were obtained (d).

on a carboxylate SAM.[11] This striking orientation was tentatively attributed to a coincidence of symmetry between the sixfold axis of the MIL-88B crystal lattice and the approximately hexagonal symmetry of the SAM–liquid interface (see Figure 4, inset, showing the MIL-88B lattice).

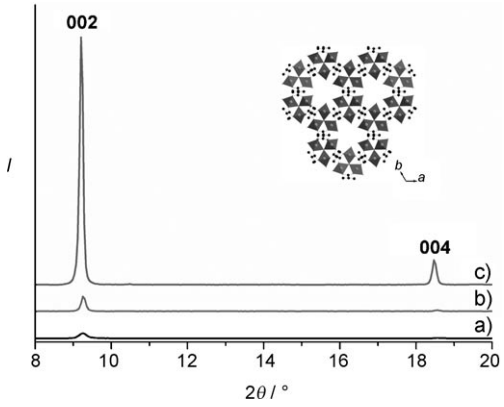

Figure 4. X-ray diffraction data (background-corrected) of Fe-MIL-88B_NH_2 produced from PEG (M_w = 20000) (a), from PEG (M_w = 100,000) (b), and from PEG (M_w = 20000) with an eight-times-higher iron(III) concentration (c). Inset: Crystal structure of Fe-MIL-88B in the [001] direction.

Moreover, as all terephthalic acid linker molecules in the MIL-88B crystal structure are oriented along [001], replacement of the COOH groups of the linker molecule by COOH groups on the SAM surface is expected to allow crystal growth in only the [001] orientation.

Subsequent time series showed that the film growth ended after about 22 h at room temperature, as indicated by nearly identical XRD intensities for immersion times between 22 h and 116 h (see Supporting Information). The influence of additional parameters, such as the concentration of $FeCl_3$ or different molecular-weight PEGs, was also investigated. The concentration of iron(III) in the PEG (20000) was increased up to eight times with respect to the initial concentration. Higher concentrations led to thicker films, as demonstrated by much higher XRD-intensities (Figure 4c). The higher ion concentrations led to the formation of small islands of crystals that were several hundred nanometers in diameter, and a thickness of 500 to 550 nm. Gaps between these islands have dimensions of about 100 nm (Figure 3c).

The molecular weight of the polymer in the metal-containing gel layer also exerts a significant influence on the nucleation and growth of the MOF crystal layer. Increasing the molecular weight of the PEG to M_w = 100000 resulted in oriented film growth with higher XRD intensities than for PEG with M_w = 20000 (Figure 4b), but the growth behavior of the crystals on the surface changed significantly. Scanning electron micrographs of this film show a homogeneous crystal layer at the bottom, covered with larger isolated, single crystals (Figure 3d). These are about 100 nm in diameter and are attributed to secondary nucleation on the first crystal layer.

As mentioned above, in a classical gel synthesis, the slow diffusion of one component into the other is the main reason for the low nucleation rates appropriate for growing single crystals. Herein we have used the gel to provide a high local concentration for efficient heterogeneous nucleation at the interface between gel and self-assembled monolayer. We propose that nucleation must proceed at this interface because we obtain near perfect orientation of the crystal layer as a function of the terminating molecular functionality of the SAM. Following nucleation, the metal ion concentration supported by complexation with the gel polymer chains will assume an increasing gradient towards the gel–solution interface, encountering an influx of the organic ligand molecules. Despite this expected gradient, further oriented growth at the solid interface can be controlled up to high local reagent concentrations. Even higher concentrations in high-molecular-weight gel layers lead to secondary oriented nucleation and growth of fewer larger crystals on the first layer. The end of the growth process is reached by the complete consumption by the linker molecules of M^{n+} stored in the gel layer. This is illustrated by the results obtained with higher iron(III) concentrations, in which case the crystal growth proceeded for a longer time, leading to thicker films. These findings illustrate the enormous potential of gel layers for the controlled oriented nucleation of crystalline phases at solid interfaces.

In summary, we have demonstrated that the newly developed gel-layer approach enables the synthesis of different oriented MOF structures on functionalized gold surfaces at room temperature. Strikingly, very homogeneous thin films of flexible Fe-MIL-88B_NH_2 were obtained in unique [001] orientation on COOH-functionalized SAMs. The MOF crystal layer thickness is tunable with the iron(III) concentration in the gel layer. Films grown on surfaces from PEG (20000) gel show both excellent lateral and apical homogeneity. Due to its high adaptability to different MOF synthesis procedures, we anticipate that the gel approach will be a powerful method to grow homogeneous thin films of many other flexible and non-flexible MOF structures. The results presented are promising for future applications of functional nanoporous thin films with controlled channel orientations. In view of the great flexibility and the new level of control in oriented thin film synthesis, we expect the generation of thin films from gel layers to become an important method in materials synthesis.

Experimental Section

SAM-functionalized slides (1 × 1.3 cm) were loaded with a gel layer of 50 % w/v poly(ethylene glycol) (M_w = 20000) in a 1:1:1 mixture of DMF/EtOH/H_2O, containing either copper(II) nitrate or iron(III) chloride at a defined concentration. Afterwards, the appropriate solution of either H_3BTC or NH_2-H_2BDC was carefully poured on top of the gel layer (for further details, see the Supporting Information).

Received: March 21, 2010
Published online: August 20, 2010

Keywords: crystal growth · gels · metal–organic frameworks · microporous materials · thin films

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