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Patterned Growth of Metal-Organic Framework Coatings by Electrochemical Synthesis

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In recent years, research interest in porous metal organic frameworks (MOFs) has risen tremendously.[1] Although most efforts have been focused on the synthesis and elucidation of new crystal structures, the broad potential of these microporous solids with unique properties is clear in areas such as gas storage,[2] molecular separation,[3] sensing,[4] etc. These applications are generally based on the use of MOFs as bulk powder. To fully exploit the potential of these new materials for membranes, sensors, and integration with microelectronics, we should preferably grow MOF crystals as patterned thin films or coatings. Conventional seeding methods as used in the growth of zeolite thin films[5] prove difficult because stable colloidal MOF solutions are not readily available.[6,7] Most previous studies of MOF films focused on the surface chemistry of the substrate. Film growth of MOF crystals was ensured by the surface affinity of the metal ion or the organic ligand constituting the framework, either by exploiting the inherent surface chemistry of the substrate[7] or by introducing functional groups as self-assembled monolayers[8−12] or as defects.[13]

Very recently, microwave heating of a conductive coating on top of a substrate was also proven to induce surface growth of MOFs.[14]

In this article, we demonstrate an electrochemical method as an effective and versatile means of growing functional MOF coatings. Thus, the applied voltage serves as a means to synthetize MOF crystals rather than to investigate their properties, as was done in previous studies.[15,16] The electrochemical synthesis of MOFs, originally pioneered by researchers at BASF,[17] enables a salt-free and continuous production, which is a major advantage in an industrial environment. The principle is based on supplying one MOF building block, the metal ion, by anodic dissolution to a synthesis solution that contains the organic ligand and a conduction salt. Careful modification of the conditions used to electrochemically produce bulk MOF material enables the preparation of thin films.

The well-known MOF structure $[Cu_3(BTC)_2]$[18] was chosen to illustrate the electrochemical formation of coatings on pure copper electrodes, although the presented method potentially extends to other structures as well.[17] This MOF consists of Cu^{II} ions held together by the tridentate ligand 1,3,5-benzenetricarboxylic acid (BTC). By applying an anodic voltage to the copper electrode, Cu^{II} ions were introduced into the synthesis solution containing BTC and methyltributylammonium methyl sulfate (MTBS) as a conduction salt. It was found that densely packed films of $[Cu_3(BTC)_2]$ crystals are easily prepared electrochemically and that thin film X-ray diffractograms (see Figure S1 in the Supporting Information) agree well with those of a conventionally prepared reference sample and with literature data.[18] It was observed that crystal size can be tuned over a wide range (2−50 μm) by simple alterations of the synthesis conditions (Figures 1A−C). Because the films are approximately one crystal thick, the thickness can be varied accordingly. Increasing the voltage from 2.5 V up to 25 V provides a higher concentration of metal ions near the surface and yields coatings of smaller crystals, as expected from nucleation theory. On the other hand, adding more water to the synthesis mixture slows down crystal formation and yields larger crystals. Under typical synthesis conditions (as for the sample in Figure 1B) around 20−25% of the dissolved copper is incorporated in the MOF crystallites constituting the coating. Although not the goal

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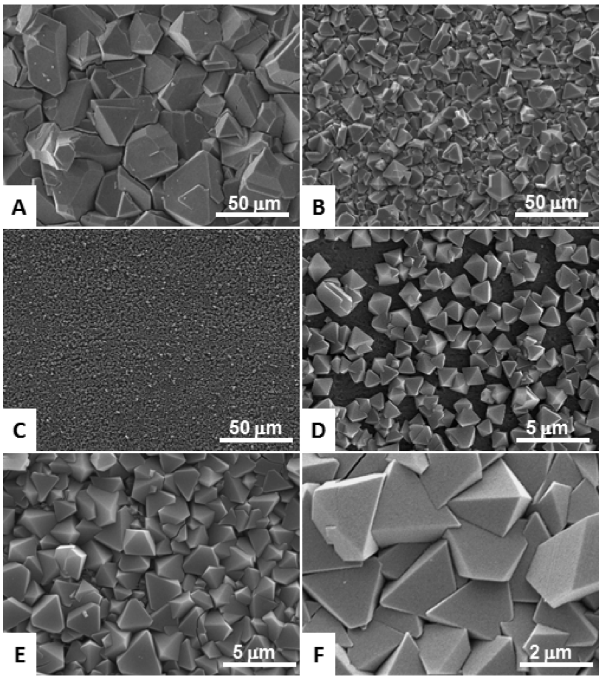

Figure 1. Electrochemical growth of $[Cu_3(BTC)_2]$ on copper anodes. Synthesis conditions were varied as indicated. (A) 50:50 water:ethanol, 2.5 V, 30 min. (B) 25:75 water:ethanol, 2.5 V, 10 min. (C) 25:75 water:ethanol, 25 V intermittently (block wave; 0.5 Hz), 15 s. (D) detail of (C) showing gaps between crystals. (E) 25:75 water:ethanol, 25 V intermittently (block wave; 0.5 Hz), 45 s. (F) detail of (E) showing highly intergrown $[Cu_3(BTC)_2]$ crystals filling in the gaps.

of the present paper, it is envisioned that increasing the efficiency is feasible by simple strategies such as increasing the ligand concentration in the synthesis solution.

Filling of the gaps in the coating seems an intrinsic property of electrochemical growth as exposed metal substrate serves as a building block reservoir rather than just as a possible anchoring point. Figure 1D−F and Figure S2 in the Supporting Information illustrate how the gaps between small $[Cu_3(BTC)_2]$ crystallites, exposing bare copper, are quickly sealed by highly intergrown crystals when synthesis time is prolonged. In contrast, film growth by other procedures reported thus far relies on the supply of both the metal ion and the organic linker from the synthesis solution.[7−14] In addition, nucleation is less likely to occur on top of the already formed crystals, and hence "piling up" of crystals is avoided. The roughness of the coatings is directly related to the size and degree of monodispersity of the composing crystallites and increases with increasing crystallite size. Typical differences in height across a 20 μm thick film are around 4−5 μm, whereas for coatings of only 2 μm thickness, height variations are typically less than 1 μm.

Besides offering the advantage of self-completion, the electrochemical synthesis is also remarkably fast. The growth times are much shorter than the several days required for repetitive growth cycles[11,12] or for preparing supersaturated growth solutions[7−10] typically employed in other methods. Furthermore, the moderate conditions used and the absence of microwave irradiation make electrochemical synthesis a likely candidate for integration of MOFs with delicate microelectronics.

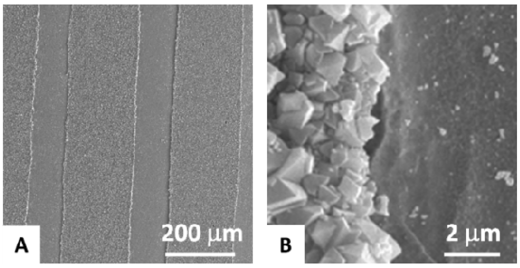

Figure 2. Electrochemical growth of $[Cu_3(BTC)_2]$ on patterned copper. (A) Copper tracks covered with electrochemically grown MOF. (B) Detail of a track edge in (A) showing the growth of MOF crystals strictly limited to the underlying pattern.

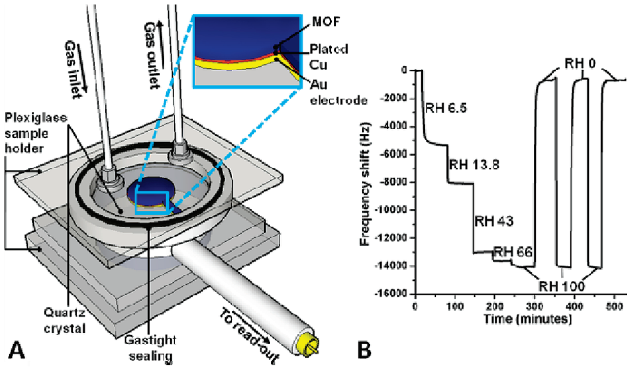

Figure 3. Electrochemically grown $[Cu_3(BTC)_2]$ coatings in QCMB measurement of water adsorption. (A) Schematic representation of the setup. (B) Signal upon adsorption of water from nitrogen streams at different RH values illustrating reversibility and reproducibility.

An indispensable property of films that are to be incorporated in functional devices is patterned deposition. The possibility of electrochemically growing $[Cu_3(BTC)_2]$ crystals on an underlying copper pattern is illustrated by using the tracks on a printed circuit board (Figure 2). Film formation takes place in the same way as on pure copper anodes and is strictly limited to the areas covered by copper.

This approach enables the incorporation of MOFs as a functional coating in microelectronic devices using standard lithographic techniques combined with electrochemical synthesis.

The possibility of using electrochemically synthesized MOF coatings integrated with sensitive measuring devices is illustrated by monitoring water vapor adsorption in a $[Cu_3(BTC)_2]$ thin film grown on top of a quartz crystal microbalance (QCMB). QCMB measurement relies on the change in vibration frequency of a piezoelectrically driven quartz crystal with adsorbed mass. This technique has previously been used to illustrate the potential of zeolite thin films in humidity and organic vapor sensing[5,19] and was recently extended to MOFs.[20] QCMB crystals can be coated with $[Cu_3(BTC)_2]$ by first plating a layer of metallic copper on the gold top electrode and subsequently forming the MOF structure by electrochemical synthesis

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(see Figure S3 in the Supporting Information). A QCMB crystal prepared in such a way was incorporated in a gastight measurement cell as shown in Figure 3A. A nitrogen flow of stepwise increasing relative humidity (RH) was introduced into the cell while recording the QCMB output signal resulting from water adsorption in the [$Cu_3(BTC)_2$] layer (Figure 3B). It is clear that changes in relative humidity can be monitored in this way and that the signal is highly reproducible upon cycling between dry and water-containing nitrogen flows. The water sorption capacity of the films was found to be 25−30 wt %, which agrees with values reported in literature[18] and indicates free pore access. The expected color changes on adsorption and desorption of water were observed through the transparent holder. Plotting of the total mass adsorbed as a function of the relative humidity produces an isotherm with clear saturation behavior at high RH values (see Figure S4 in the Supporting Information).

In summary, we have demonstrated an electrochemical procedure for the self-completing growth of uniform MOF thin films that allows for tuning the size of the densely packed crystallites. Patterned coatings produced in this manner might prove useful in the integration of MOF materials with functional devices. The practical application of these films was conceptualized by QCMB monitoring of the adsorption of water vapor in the MOF layer.

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Supporting Information Available: Experimental procedures, thin film and powder XRD diffractograms (Figure S1), SEM micrographs showing a cross-section through coatings after different synthesis times (Figure S2), ESEM micrograph of [$Cu_3(BTC)_2$] coating on QCMB crystal (Figure S3), plot of mass adsorbed on coated QCMB crystal in function of RH (Figure S4) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.