Patterned film growth of metal–organic frameworks based on galvanic displacement†

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A new method based on patterned metallization and galvanic displacement is demonstrated to easily deposit patterned thin films of the metal–organic framework [Cu₃(BTC)₂].

Because of their well-defined cavities of molecular dimensions and their large internal void space, microporous crystalline solids such as zeolites and metal–organic frameworks (MOFs) can be used for gas storage,1 as catalysts2 and as selective sorbents.3 In addition to these applications that are based on solids synthesized and applied as a bulk material, the preparation of microporous thin films of these materials adds to their applicability as sensor coatings, membranes, hosts for supramolecular organization, etc. While for zeolite thin films a large body of work exists concerning their preparation and application,4,5 demonstrating the potential of the newer MOF materials in this area will rely on dependable ways to spatially control MOF deposition.6,7 In recent literature, several ways to deposit thin films of MOFs have been reported which can be divided into in situ, ex situ and seeding methods. In ex situ8,9 and seeding methods10–14 film formation is based on the deposition of previously prepared (nano)crystals on a surface, followed by a secondary growth step in the case of seeding. In contrast, in situ methods rely on the surface chemistry of the substrate to promote preferential nucleation and/or attachment of nuclei to the surface to achieve film growth. Generally, the surface affinity of the metal ion or the organic ligand constituting the framework is enhanced in this case by introducing functional groups as self-assembled monolayers15–21 or as defects.22 Recently, we reported a different, electrochemical type of in situ growth in which the structural metal ion is supplied by anodic oxidation of the metallic substrate instead of being supplied together with the ligand from solution.23

When considering the growth of patterned thin films to only coat specific parts of e.g. a sensor surface, MOF formation should not only be limited to the surface but spatial control should also be exerted within the surface plane. In situ growth methods seem more suitable to this aim since surfaces can be functionalized or metallized in a patterned way. This results in patterned patches of, respectively, preferential nucleation/attachment sites or metal ion reservoirs, enabling the patterned growth of thin MOF layers.16–18,23,24 While the electrochemical method can rely on well-known and widely applied processes to deposit metallic patterns, anodic oxidation driven by an external power supply requires continuous electrical contact of the complete metallic pattern with the power source. This condition complicates coating of non-interconnected patterns. Here, we demonstrate an alternative electrochemical method based on galvanic displacement for coating metallic patterns with MOF crystals, regardless of their interconnectivity.†

Galvanic displacement takes place when a solution containing ions of a more noble metal is contacted with a less noble metallic substrate. Due to the difference in reduction potential, the more noble metal is reduced and plated on the substrate. The metallic substrate itself is oxidized, as a result of which cations are released. Industrially, this process is widely used to deposit metal films with high purity and substrate adhesion.25 For depositing patterned MOF coatings, the advantage of galvanic displacement lies in the localized supply of metal ions by oxidation of an underlying metallic pattern without the need of ensuring electrical contact with an external power supply. Metal ions set free this way serve as building blocks for the MOF coating growing on top of the metallic pattern.

The concept described above is illustrated for the well-known MOF [Cu₃(BTC)₂]. The crystal lattice of this structure consists of CuII ions linked together by 1,3,5-benzenetricarboxylate (BTC) ligands.26 Thin films of [Cu₃(BTC)₂] have previously been demonstrated as active coatings in various mass-based sensors.23,27,28 The process of depositing patterned [Cu₃(BTC)₂] films by galvanic displacement is illustrated in Fig. 1.† First, a pattern of metallic Cu is deposited on a glass substrate, in the present case by thermal evaporation using a shadow mask. In a second step, a solution of silver nitrate and H₂BTC in dimethyl sulfoxide (DMSO) is spincoated on top and the sample is heated at 353 K. By galvanic displacement, CuII ions are released while silver ions are reduced. The CuII ions react with the H₂BTC molecules in solution to yield [Cu₃(BTC)₂] during evaporation of the solvent. It was previously shown that high quality [Cu₃(BTC)₂] is obtained from CuII and H₂BTC in DMSO as a synthesis solvent under evaporative conditions.29 After evaporation, samples are kept in ethanol. Note that to confine MOF growth to the metallic pattern, the spincoated solution should preferably wet the metal regions and have lower affinity for the bare glass in between them. To achieve this difference in wettability, the

glass surface was treated with chlorotrimethylsilane before vapour deposition of the metallic pattern. The effect of this treatment is shown in Fig. 2. For clarity, DMSO was stained with methylene blue. While DMSO does not preferentially wet the metallic pattern on an untreated, silanol-terminated glass surface, this clearly is the case after silanization of the surface.

Fig. 3 shows the result of coating a pattern of 50 × 50 μm² copper squares by galvanic displacement. It is evident that relatively large areas can be modified in one step using this method. The edges of the squares are sharply defined and crystallite deposition is strictly confined to the underlying metallic pattern (Fig. 3B). The coating on each square is homogeneous and consists of small intergrown octahedral \([Cu_3(BTC)_2]\) crystallites (100–200 nm) (Fig. 3C). Note that in the present case homogeneous MOF films are not obtained by the presence of preferential nucleation/attachment sites on the surface, but rather by a uniform release of the structural metal ion across the metallic substrate. The adherence of the crystallites to the metal underneath is quite strong as evidenced by the resistance to bursts of sonication (see Sample preparation). This strong connection exists because of the roughness of the metallic silver deposited under the present conditions, which serves as an anchorage for the MOF crystallites. As expected, the XRD reflection pattern of coated samples evidences both the presence of \([Cu_3(BTC)_2]\) and metallic silver (Fig. 4) whereas before applying the silver nitrate containing solution only Cu is detected (Fig. S1, ESI†). MOF crystallites in the coating are randomly oriented, as can be concluded from the presence of diffraction peaks corresponding to different crystallographic orientations. The absence of the Cu signal after galvanic displacement confirms complete coverage of the underlying metallic pattern.

In summary, we demonstrated how patterned metallization and galvanic displacement can be combined to deposit patterned thin films of MOFs as illustrated for the case of \([Cu_3(BTC)_2]\). The combination of these established methods could advance the ease of processing MOFs for application in sensors and other thin film devices.
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Notes and references

‡ Sample preparation: microscope cover glasses (Knuttel Gläser, borosilicate D 263) were silanized by treatment in an 8 wt% solution of trimethylchlorosilane in dichloromethane. After 24 h, cover glasses were rinsed with dichloromethane and dried in argon. Copper metal patterns (150 nm layer thickness) were deposited on the silanized cover glasses using thermal vacuum evaporation at a base pressure of approximately 10⁻⁴ mbar. High purity copper wire was used after washing with dilute HNO₃ to remove oxide impurities. A TEM grid of Agar, 300 mesh) with square perforations of 50 × 50 μm was used as a shadow mask resulting in a area of 2 \( \times \) 2 mm² patterned with copper squares. Approximately 100 mg of a solution of 2 g AgNO₃ and 2 g H,BTC in 100 g DMSO was spincoated (Specialty Coating Systems, a linear position sensitive detector: step width 0.5 \( \times \) 1 \( \times \) squares. Approximately 100 mg of a solution of 2 g AgNO₃ and 2 g H,BTC in 100 g DMSO was spincoated (Specialty Coating Systems, Spincouter 6812, 10 s, 5000 rpm) on the copper patterns. Afterwards, samples were immediately placed in an oven at 353 K during 5 minutes. When solvent evaporation was complete, coated samples were kept in ethanol to wash away unused reagents. This was aided by sonication bursts for up to 10 minutes. No significant loss of crystallites from the metallic patches was noticed after sonication. Characterization: light microscopy was performed using a JVC TK-C1381 colour video camera coupled to a CETI stereomicroscope. XRD reflection patterns of surface samples were recorded on a STOE STADI MP in Bragg–Brentano mode (2θ = 0 geometry; CuK\( \alpha \) using a linear position sensitive detector: step width 0.5° 2θ, scan rate: 1520 s⁻¹ per step (2θ = 5–20°; Δ2θ = 0.01°). SEM micrographs were recorded using a Philips XL30 FEG after coating with Au.