Rapid fabrication of metal organic framework thin films using microwave-induced thermal deposition†

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We have demonstrated a novel method to rapidly fabricate nanoporous MOF thin films and patterns on porous alumina substrates under microwave irradiation.

Nanoporous metal–organic framework materials pioneered by Yaghi and co-workers[1] have drawn tremendous interest due to their potential applications in gas-storage,[2] gas separation,[3] gas sensing,[4] and catalysis.[5] Metal–organic framework materials (MOF) generally consist of metal–oxygen polyhedra containing divalent (Zn^{2+}, Cu^{2+})[1] or trivalent (Al^{3+}, Cr^{3+})[6] metal cations interconnected with a variety of organic linker molecules, resulting in tailored nanoporous materials. With a judicious choice of organic linker groups, it is possible to fine-tune size, shape, and chemical functionality of the cavities and the internal surfaces.[7] This unique structural feature offers unprecedented opportunities in small-molecule separations as well as chiral separations and catalysis.[8–11]

While MOF materials are currently available in powder forms as adsorbents and catalysts, there are strong interests to fabricate uniform, defect-free films for continuous membrane-based separations, membrane reactors, and other advanced applications such as optical, electronic, and magnetic applications.[12–16] Despite the current immense investigations into the chemistry of MOF materials,[17] there have been only a few reports on the growth of MOF crystals on atomically smooth non-porous solid surfaces such as silicon wafers to date.[13–15] Among other issues, one major obstacle to growing MOF films on substrates is the organic linkers in MOF materials, which make the materials unique and extremely versatile as described above, yet can be problematic.[13] These organic linkers typically do not provide additional linkage groups that can form bonds with linkage groups on the surface of the supports (*i.e.*, hydroxyl groups in case of metal oxides). As a result, the surfaces of the support typically had to be either chemically modified or electro-statically compatible (*e.g.*, Al_2O_3 with an isoelectric point (IEP) of 9.1) in order to grow MOF films.[13,14,18] One exception is the films of a layered MOF, $[Zn_2(bdc)_2(dabco)]$ (bdc = benzene dicarboxylate, dabco = 1,4-diazabicyclo[2.2.2]octane), on bare SiO_2 (IEP $\approx$ 2) substrates through hydrogen bonds with surface hydroxyl groups and the amine groups of dabco.[16] In addition to the preparation of the substrates, laborious processing steps were required to prepare supersaturated growth solutions, thereby typically taking several days.[13] Besides, none of the previous reports addressed the binding strength of MOF crystals on the substrates, which are of critical importance for practical applications.

Microwave-assisted homogeneous as well as heterogeneous nucleation of zeolites and their derivatives have been proved to be an effective way to prepare powders and films of zeolitic materials.[19,20] Rapid production of metal–organic framework crystals *via* microwave-assisted solvothermal synthesis has been recently reported by a couple of research groups.[21–23] Carbon nanotubes[24] and silicon nanowires[25] were grown using microwave-assisted chemical vapor deposition processes. However, there have been no reports on the fabrication of MOF films on porous support under microwave irradiation.

Here we report a novel method, microwave-induced thermal deposition (MITD), to prepare MOF thin films on porous substrates in a facile manner. To prove the versatility of our method, the selective patterned deposition of MOF-5 crystals as well as a multi-layer film (an MOF-5/zeolite silicalite-1 film) on a substrate are presented.

Experimental details are provided in the ESI.† Briefly, the MOF-5 precursor solution was prepared according to a previously reported procedure.[22] Substrates (nanoporous anodized alumina discs, Anodisc®, Whatman Co.) coated with various conductive thin films were then placed vertically in vials containing the precursor solution and MOF-5 crystals were grown under microwave irradiation in a domestic microwave oven with 500 W power for 5–30 seconds. Anodisc® substrates were chosen as mechanical supports with negligible transport resistance to gas molecules, which is important for potential applications of MOF films in gas separation. The resulting films and powders were thoroughly washed, dried, and stored in a desiccator for analysis.

Fig. 1 shows SEM images of MOF-5 crystals grown on three different substrates prepared for 30 seconds under microwave

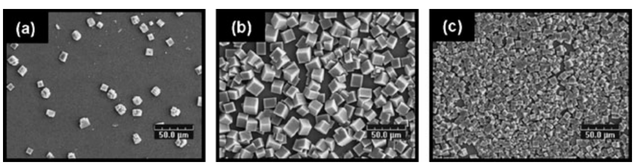

Fig. 1 SEM images of MOF-5 grown (a) on a bare AAO, (b) on an amorphous carbon-coated AAO, and (c) on a graphite-coated AAO. MOF-5 were grown for 30 seconds under microwaves.

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irradiation: a bare anodized aluminium oxide substrate (hereafter, AAO), an amorphous carbon-coated AAO (hereafter, C-AAO), and a graphite-coated AAO (hereafter, G-AAO). Hereafter, MOF-5 crystals grown on AAO, C-AAO, and G-AAO are denoted MOF/AAO, MOF/C-AAO, and MOF/G-AAO, respectively. There are several observations to make. First, the kinetics of the heterogeneous nucleation and growth of MOF-5 crystals on substrates are enhanced dramatically when there are thin conductive layers such as amorphous carbon or graphite (see Fig. 1b and c as well as Fig. S1 in the ESI†) as compared to that on an uncoated substrate. It typically takes about 20–30 seconds to prepare well-packed MOF-5 films on the substrates with conductive layers. This rapid deposition makes a sharp contrast with the typical preparation time of several days with previous methods.[13–15] It is also important to note that our method requires neither organically modified surfaces nor atomically smooth surfaces, thus providing a viable route to prepare MOF thin films and membranes. We speculate that this surface dependency results mainly from the fact that microwaves interact differently with materials with different electric and/or dielectric properties.[26] It is surmised that the rapid temperature rise at the conductive surfaces *via* Joule heating (*i.e.*, electron–phonon interaction) upon the absorption of microwave energy on the surfaces causes a substantial increase in the rate of the heterogeneous nucleation and growth of MOF crystals. This microwave-induced thermal effect is obviously an additional element along with other typical factors affecting heterogeneous nucleation and growth such as surface properties (chemical and physical). However, the rapid increase in the surface temperature under microwaves is found to be critical in order to prepare MOF-5 films on G-AAO since we were not able to grow MOF-5 films on G-AAO under conventional solvothermal synthesis conditions. We have also grown MOF-5 films on substrates coated with Au/Pd, showing similar enhancement of the kinetics of heterogeneous nucleation of MOF-5 crystals (see Fig. S2 in the ESI†).

Second, MOF/G-AAO shows smaller and more densely-packed MOF-5 crystals as compared to MOF/C-AAO and MOF/AAO. This smaller size and higher number density of MOF-crystals on G-AAO can be explained by the rapid formation of more nuclei on the graphite surface under microwaves than on the amorphous carbon and the bare alumina surfaces, followed by their mass transfer-limited growth. The films grown on G-AAO also display some degree of inter-growth of the crystals, implicating a possibility to prepare continuous, well inter-grown films *in situ* under microwaves.

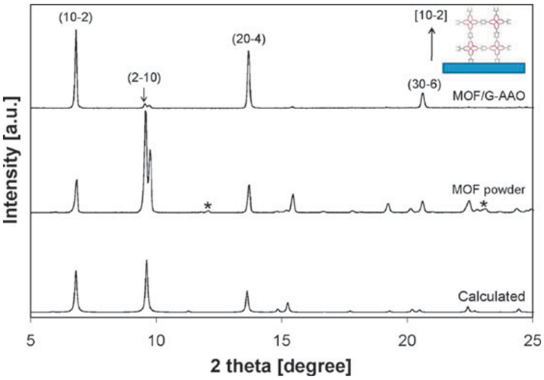

Fig. 2 XRD pattern of MOF-5 thin film grown on G-AAO as compared with that of MOF-5 powder prepared under MW and a calculated pattern based on single crystal MOF-5 structure (space group: $R\bar{3}m$).[27] *: unknown phase.

Finally, one can observe in Fig. 1c that the MOF-5 film grown on G-AAO shows an out-of-plane preferred orientation for the MOF-5 crystals with the [10-2] direction perpendicular to the substrate (see the inset illustration in Fig. 2). It is worth mentioning that different synthesis methods yield MOF-5 crystals with different crystal systems (cubic *vs.* trigonal) mainly due to the presence of Zn species in the cavities and lattice interpenetration.[27] However, the [10-2] direction in a trigonal system is the same as ⟨100⟩ in a cubic system in that the channels are perpendicular to the substrates. The orientation of the MOF-5 crystals on the G-AAO is confirmed by X-ray diffraction with a reflection sample geometry as shown in Fig. 2. Unambiguous evidence of the out-of-plane preferred orientation is provided by comparison of the [10-2] and [2-10] reflections. The crystallographic preferred orientation,[28,29] CPO, for these reflections is in the range of 20–50, indicating strong orientation. We are speculating that the oriented growth might be triggered by the addition of carboxylic groups on the surface defect sites or edges of graphite flakes caused by intense microwave Joule heating in combination with preferred deposition of benzene dicarboxylic acids, the organic linker, on the aromatic carbon six rings of the graphite sheets. We are currently investigating the nucleation and growth of a MOF-5 crystal on a graphite surface.

Strong adherence of MOF crystals on the support surface is vital to obtaining mechanically robust MOF thin films.[30] The binding strength of MOF-5 crystals on G-AAO was tested using a sonication method.[31] As shown in Fig. 3, about 80% of the MOF-5 crystals remain attached on the surface even after 1 h of sonication despite the degradation of some crystals due to the intense sonication (see Fig. 3c and the inset),

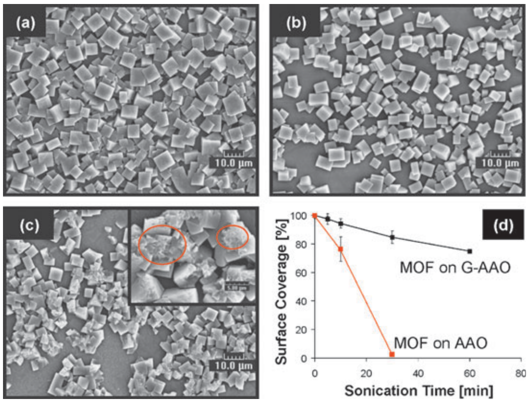

Fig. 3 Binding strength of MOF-5 crystals on G-AAO and AAO under sonication: SEM images of MOF-5 films on G-AAO treated under sonication for (a) 0 min (as-prepared), (b) 10 min, and (c) 60 min, and time-dependent surface coverages (d). The coverage data were obtained by examining image contrast between MOF crystals and substrates using Adobe Photoshop. The data were normalized to the initial coverages.

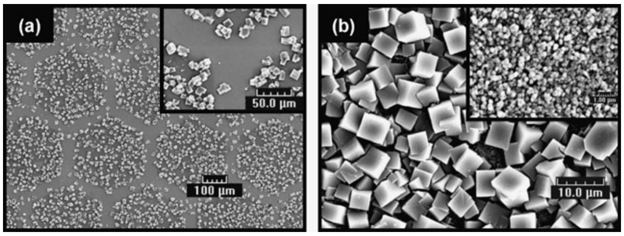

Fig. 4 SEM images of (a) patterned growth of MOF-5 crystals on patterned C-AAO substrates using a TEM grid and (b) a multi-layer MOF/silicalite-1 on Au-AAO. Inset image in figure (b) is from the underlying silicalite-1 layer.

suggesting strong bonds (likely covalent) formed between MOF crystals and the graphite. It is speculated that carboxylic groups of the organic linker molecules might be covalently anchored on the surface defect sites or edges of graphene sheets caused by intense microwave Joule heating. In contrast, all of the MOF-5 crystals grown on a bare AAO were detached after only 30 minutes of sonication (see Fig. 3d and ESI Fig. S3†), thereby indicating weaker binding of MOF-5 crystals on a bare AAO (possibly electrostatic).[14] Further study is needed to elucidate the nature of the binding.

The ability to deposit MOF materials in patterns is often required for advanced applications such as sensors and electronic/optical devices. Fig. 4a show the patterns of MOF-5 crystals prepared on carbon-patterned AAO substrates within 30 seconds, demonstrating the ability of our method to generate patterns in a rapid manner. Carbon-patterned substrates were made by thermally evaporating the carbon source on to a copper TEM grid placed on AAO. As can be seen, most of the MOF-5 crystals were grown on those areas where carbon was deposited. A multi-layer film of two different materials was also prepared as shown in Fig. 4b. In short, a silicate-1 thin film was deposited on an Au-coated AAO under microwaves and then a thin graphite layer was applied onto the silicalite-1 film, followed by a MOF-5 layer grown under microwaves. The ability to rapidly fabricate multi-layer thin films has a significant implication in developing membranes with multiple separation capabilities. For instance, the first layer separates molecules based on thermodynamics and the second layer based on kinetics. The ability to deposit MOF-5 crystals in patterns and to grow a multi-layer film in a facile manner proves the versatility of the microwave-induced thermal deposition technique.

In summary, we have demonstrated a novel method to rapidly fabricate nanoporous MOF thin films and patterns on porous alumina substrates under microwave irradiation. Thin layers of conductive materials such as amorphous carbon, graphite, and other metals such as Au were found to drastically enhance the kinetics of heterogeneous nucleation and growth of MOF-5 crystals. The enhancement of the kinetics was attributed to the increased temperature of the conductive layers due to resistive Joule heating generated by the absorption of microwave energy by the conductive surfaces. The liquid-phase microwave-induced thermal deposition process can potentially open up new possibilities to rapidly fabricate thin films and patterns of various materials on substrates that can be thermally activated in solutions.

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