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Tuning Omniphobicity via Morphological Control of Metal−Organic Framework Functionalized Surfaces

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Supporting Information

ABSTRACT: Fabrication of microstructures for imparting omniphobicity to a surface generally requires the use of lithographic techniques and specialized equipment. We report instead a simple strategy for the synthesis of microstructured surfaces via metal−organic framework (MOF) self-assembly. Our method allows us to localize epitaxial growth of MOF at the tips of needle crystals to create mushroom-shaped structures, thus conferring re-entrant textures to the MOF-functionalized surfaces. These structures synthesized via wet chemistry were found to have omniphobic properties due to the resulting re-entrant texture.

Metal−organic frameworks (MOFs) have emerged as a chemically versatile class of materials,[1] owing to significant advances in synthetic control over MOF functionality and topology.[2,3] Recent research emphasizing tuning of MOF crystal size and morphology[4,5] has allowed for yet newer ways of tailoring MOF properties for specific functions, such as biomedical imaging[6] and chemical sensing.[7] MOF crystal morphology can be controlled during synthesis via coordination modulation,[8] or by employing microemulsions whereby micellar shape determines the resulting crystal shapes.[9] Another area that has seen significant progress is the growth of MOF on solid supports,[10] allowing for control over crystal orientation and surface morphology.[11−14]

An important application of surface morphological control is in the fabrication of microstructured surfaces to create superhydrophobic material.[15−17] Superhydrophobicity, whereby a surface has a water contact angle of more than 150°, is a phenomenon observed in nature, with the lotus leaf being a well-known example.[18] Typically, high liquid repellence is achieved by surfaces with micro or hierarchical roughness which allows for trapped air between a liquid droplet and its supporting surface.[19] Cohen et al. have demonstrated surfaces that display superomniphobicity, where the surfaces are both superhydrophobic and superoleophobic,[17] through the use of microstructured surfaces with re-entrant curvature. These structures help to stabilize the metastable Cassie state,[19] preventing the irreversible transition to the wetting Wenzel state.[20] However, these surfaces were fabricated by relatively complicated top-down processes. Further, while various examples of superhydrophobic MOFs have been reported,[21,22] to the best of our knowledge, there has been no report of oleophobic MOFs. We show here a facile synthetic strategy to introduce re-entrant morphology to MOF-functionalized surfaces without resorting to top-down lithographic methods, and thereafter demonstrate their omniphobicity.

Through coordination modulation, the crystal aspect ratio of anisotropic MOFs such as $[\{Cu_2(ndc)_2(dabco)\}_n]$[8b] and NH_2-MIL-53(Al)[8c] can be controlled, allowing for the synthesis of nano- and microscale rods and needles. NH_2-MIL-53(Al) is of particular interest as the amino group on the ligand allows for easy postsynthetic modification (PSM) via reaction with perfluorooctanoyl chloride to lower the MOF surface energy, thus significantly increasing MOF hydrophobicity.[21,22] Furthermore, Caro et al. illustrated the growth of oriented ZIF-7 and ZIF-8 films on alumina membranes where the oriented growth was attributed to evolutionary screening as described by the van der Drift growth model.[14] We postulated that NH_2-MIL-53(Al) microneedles could similarly be grown on a substrate in an aligned fashion perpendicular to the support. Through this, a rough surface with interstices between the needles for trapping air would be created.

Reaction of 2-aminoterephthalic acid with an anodic aluminum oxide (AAO) membrane (13 mm diameter) supported on a glass slide (Figure 1) under hydrothermal conditions yielded yellow block microcrystals of NH_2-MIL-53(Al) on both sides of the membrane surface (Figure 2a, see Supporting Information for experimental details). The AAO functioned as both a solid support as well as an Al^{3+} source for MOF growth. Repeating the reaction with acetic acid added as a modulator resulted in patches of NH_2-MIL-53(Al) microneedles with a spiny 'microflower' morphology (Figure 2b). Interestingly, these needles showed decreased alignment

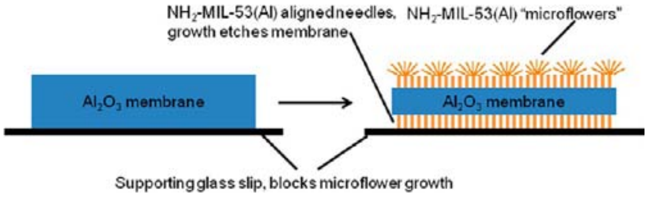

Figure 1. Graphical representation of how NH_2-MIL-53(Al) is grown on an anodized aluminum oxide (AAO) membrane.

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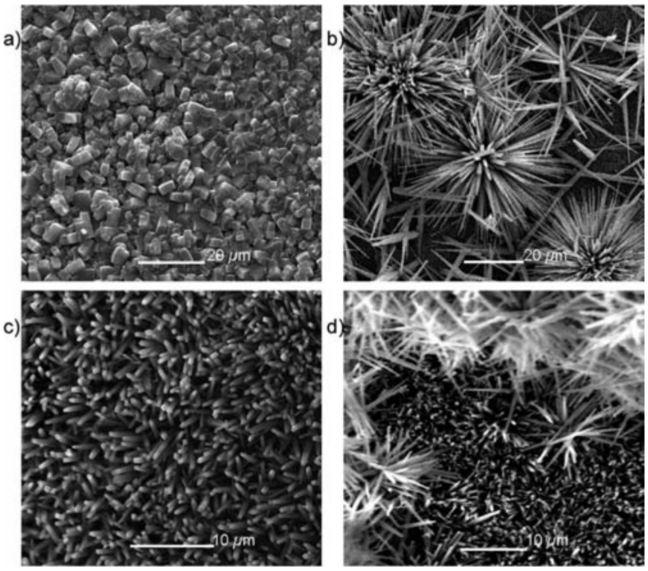

Figure 2. SEM images of AAO membrane with (a) NH_2-MIL-53(Al) microcrystals from reaction of AAO with 2-aminoterephthalic acid without modulator, (b) NH_2-MIL-53(Al) microflowers reaction of AAO with 2-aminoterephthalic acid with modulator (AAO is visible beneath the microflowers), (c) NH_2-MIL-53(Al) aligned microneedles grown on seeded AAO surface supported on glass slip with modulation, (d) layers of NH_2-MIL-53(Al) microflowers on aligned needles grown on exposed AAO surface.

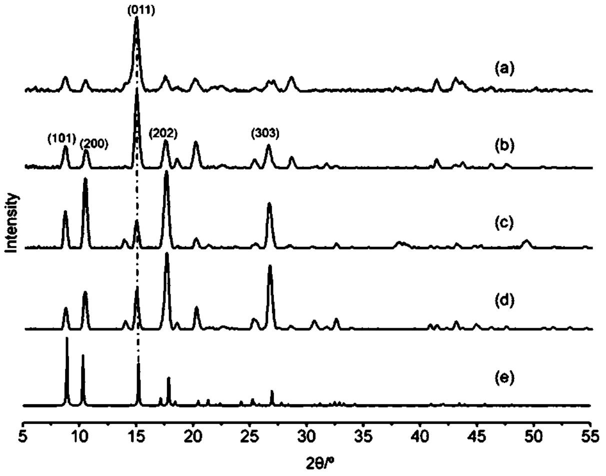

Figure 3. X-ray diffraction pattern (normalized to the highest intensity) of NH_2-MIL-53(Al) (a) micromushrooms on alumina membrane, (b) aligned needles grown on alumina membrane, (c) microcrystals grown on alumina membrane, (d) randomly oriented powder, (e) simulated from MIL-53(Al) powder.[24]

toward the edges of the patches where the needle growth was sparse and increased alignment toward the patch centers where there was a higher density of needles. We reasoned that denser coverage of microneedles would therefore lead to better alignment through evolutionary screening.[14] This was achieved by seeding the AAO membrane with NH_2-MIL-53(Al) nanoparticles prior to hydrothermal reaction, similar to the reactive seeding method performed by Jin et al.[23] This resulted in aligned microneedles (Figure 2c) on both sides of the membrane.

The side of the membrane in contact with the glass substrate during the hydrothermal reaction sported only a monolayer of aligned needles, as the glass served to block further nucleation and growth of additional MOF crystals on the needle tips (Figure 1). In contrast, the exposed side displayed multiple, uneven microflower layers on top of the aligned microneedles (Figure 2d, Figure S5).

The XRD patterns of NH_2-MIL-53(Al) grown on AAO without modulation (Figure 3c) and NH_2-MIL-53(Al) bulk powder (Figure 3d) were very similar, indicating a random orientation of the block microcrystals on the AAO surface. However, the XRD pattern of the densely grown NH_2-MIL-53(Al) needles (Figure 3b) showed a higher intensity peak belonging to the [011] direction, while peaks belonging to [$h0k$] directions were weaker in intensity. The main axis of the needle crystal is in the crystallographic b direction (Figure S11), which grows outward from the AAO membrane surface.

As synthesized, the NH_2-MIL-53(Al) needle-covered AAO membranes were hydrophilic and were wetted by water droplets. PSM of the MOF was performed by reacting it with perfluorooctanoyl chloride (see Supporting Information for experimental details), after which a very high static water contact angle to the membrane was obtained (>160°, Figure S10). We also found that aligned needles exhibited high contact angles with diiodomethane (~140°), but were easily wetted by hexadecane. The microflowers showed similar liquid repellence properties to the aligned needles; however, the unevenness of the surface caused large variations in contact angle measurements and hence further investigation was focused on the aligned needle side of the AAO membrane. To increase the oleophobicity of the surfaces, the possibility of introducing a re-entrant texture[17] by morphologically modifying the microneedles was explored.

Prior to PSM, the MOF covered AAO membranes would absorb water and sink when placed on an aqueous surface. However, after PSM with perfluorooctanoyl chloride, placing the modified membranes into aqueous solutions showed that they remained afloat on the solution surface, even after repeated attempts to submerge them. The modified samples are superhydrophobic; hence, the needle wetting by water should be better described by the Cassie−Baxter state[19] rather than the Wenzel state.[20] Since the interstitial air prevents the precursor solution from coming into contact with the microneedles except at their tips (Figure 4), we reasoned that it should be possible to selectively expand the microneedle tips through epitaxial MOF growth by simply floating the disc on an aqueous NH_2-MIL-53(Al) precursor solution. Although epitaxial growth at a MOF-solution interface is commonly used to synthesize hybrid MOF films,[25] as well as isoreticular MOF@MOF core−shell structures,[26] to our knowledge there has been no report of localized epitaxial MOF growth using a MOF-solution−air three way interface.

Floating the microneedle-covered disc on the surface of an aqueous solution of $Al(NO_3)_3$ and 2-aminoterephthalic acid did indeed result in the growth of new NH_2-MIL-53(Al). The additional MOF growth was unmodulated, allowing for needle tip expansion in the plane normal to the needle axis, resulting in mushroom-like caps of MOF on the needle stems (Figure 5a,b). Longer reaction times resulted in larger cap diameters as well as the extension of the caps along the lengths of the rods, leading to popsicle-like morphologies (Figure 5c). This is due to the decreasing hydrophobicity of the MOF membrane as NH_2-MIL-53(Al) grows on the needle tips, resulting in the precursor solution being able to travel further up the needle

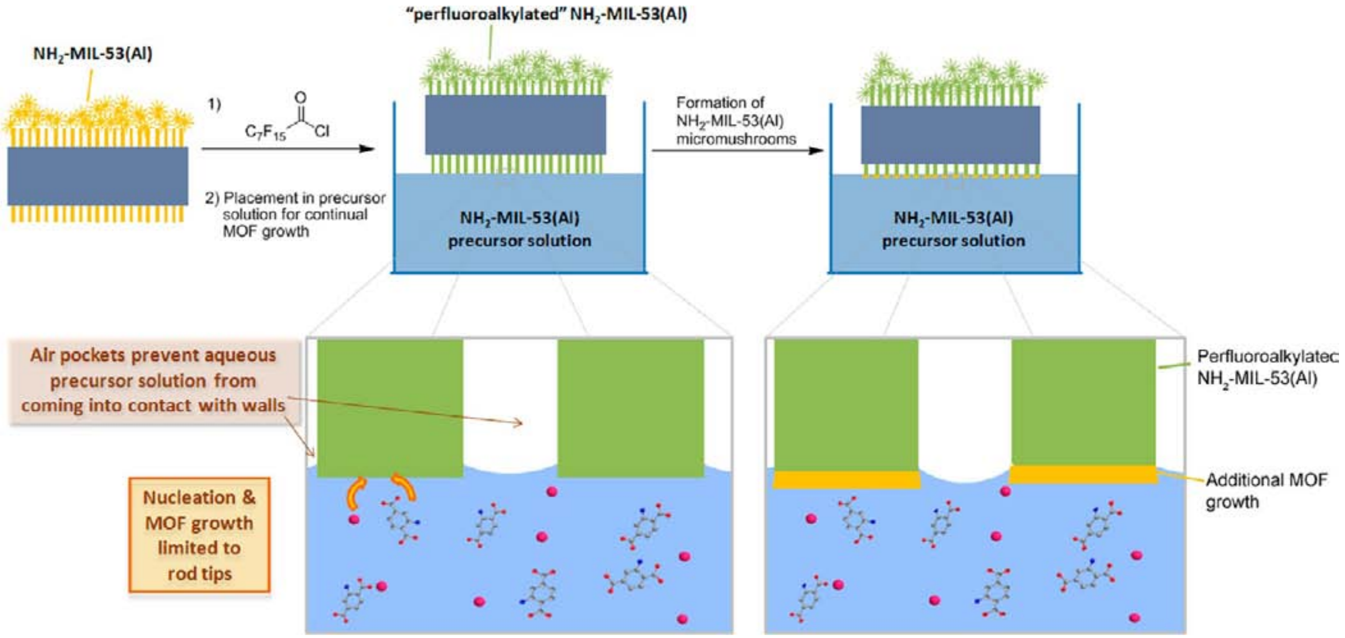

Figure 4. Graphical representation of NH_2-MIL-53(Al) micromushroom synthesis through interfacial continual growth.

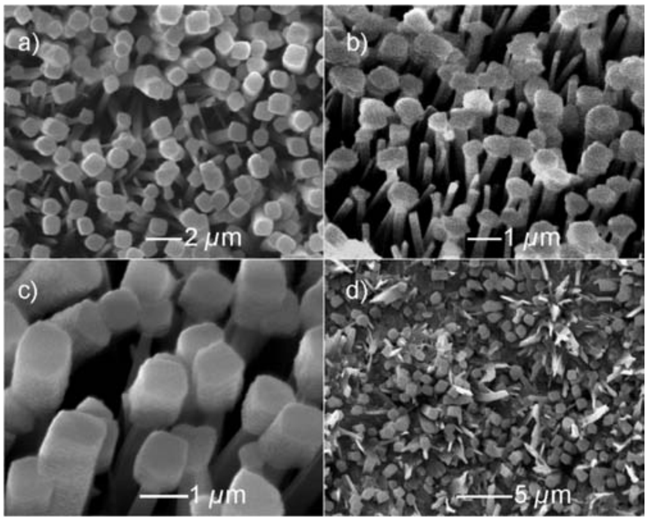

Figure 5. SEM images of (a) NH_2-MIL-53(Al) micromushrooms, (b) NH_2-MIL-53(Al) micromushrooms at 45° tilt angle, (c) NH_2-MIL-53(Al) 'popsicles' made from stacks of mushroom caps, and (d) NH_2-MIL-53(Al) film formed from fused mushroom caps.

length. The popsicles consisted of stacks of mushroom caps fused together. Further reaction led to adjacent caps fusing together, forming NH_2-MIL-53(Al) films (Figure 5d). Since the cap sizes could be controlled by varying reaction time, the growth was stopped once the caps had reached the target diameter (around 1 μm) to avoid film formation.

XRD analysis of the micromushrooms showed that the mushroom caps had the same crystallographic orientation as the needles. The relative intensity of the [011] peak was even higher after the mushroom caps were grown due to the larger surface area of the (010) plane parallel to the support (Figure 3a). The XRD as well as the SEM images support that the growth of NH_2-MIL-53(Al) on the needle tips is epitaxial and not randomly oriented. Attempts to grow nonisoreticular MOFs such as HKUST-1[27] and ZIF-8[28] on the hydrophobized needles under similar conditions were unsuccessful, which suggests the importance of epitaxy for the growth of new MOF on the hydrophobic needle surfaces.

After the surface energy of the NH_2-MIL-53(Al) mushroom caps was lowered via PSM with perfluorooctanoyl chloride, we investigated the oleophobicity of the mushroom surfaces to see if the liquid repellent properties were similar to the re-entrant textured surfaces described in the literature.[17] Prior to mushroom growth, the perfluoroalkylated aligned needles adsorbed *n*-hexadecane readily. However, after the needles were subjected to continual growth and the MOF caps had been functionalized with perfluorooctanoyl chloride, the AAO/MOF surfaces were found to be oleophobic, displaying contact angles of up to 100° with *n*-hexadecane (Figure 6; see Supporting Information for experimental details). The contact angle data of various liquids on the aligned needles and mushroom surfaces is reported in Table 1. The micromushroom morphology synthesized by wet-chemical techniques is thus comparable to the microstructures fabricated by lithographic techniques.

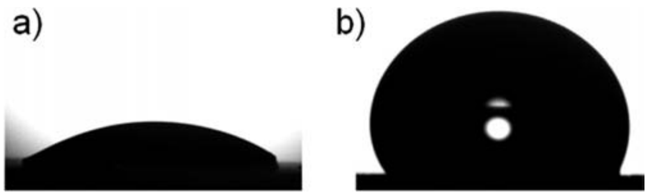

Figure 6. Contact angle of *n*-hexadecane on NH_2-MIL-53(Al) (a) aligned microneedles and (b) micromushrooms.

Table 1. Contact Angles on NH_2-MIL-53(Al) Surfaces/deg

liquid	needles	mushrooms
water	153−163	151−169
DMSO	129−150	130−150
diiodomethane	140−152	157−160
n-hexadecane	20−25	80−100

In summary, we have demonstrated a simple strategy for the synthesis of re-entrant morphologies. By taking advantage of the air pockets trapped in the interstices of a liquid repellent material, we can localize epitaxial growth during MOF self-assembly. This allows us to use wet-chemical techniques to create morphologies previously afforded only by top-down imprinting or lithographic processes. Our simple method of morphological control could also be used for the creation of other unique architectures by wet chemical methods.

ASSOCIATED CONTENT

Supporting Information

Experimental details, TEM and SEM images, contact angle data, and FTIR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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