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Understanding moisture-induced mesopore formation in metal organic framework $Cu_3(btc)_2$ using three-dimensional FIB/SEM analysis

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Metal organic framework (MOF) copper benzene-1,3,5-tricarboxylate ($Cu_3(btc)_2$ or HKUST-1) is one of the most broadly studied MOFs, considered for a diverse range of applications including gas storage and separation. Like many MOFs, HKUST-1 has a known sensitivity to water vapor, with performance in most applications degrading under ambient humidity. Prior work on the effect of moisture has focused on performance metrics or changes at the scale of the copper sites and the lattice. While it is generally appreciated that moisture leads to framework collapse, the consequences for the MOF microstructure remain largely unconsidered.

The internal structure and three-dimensional morphology of HKUST-1 particles can be examined using the focused ion beam/scanning electron microscope (FIB/SEM). While MOFs are exceptionally beam-sensitive, it is possible to get sufficiently uniform milling with 30 kV Ga-ions at low fluence rates, even at room temperature. Commercially available (BASF Basolite C300) and lab-grown HKUST-1 particles commonly have internal contrast suggestive of grain boundaries and planar defects. Based on the external morphology of the more regularly-shaped particles, many of the planar features are nominally consistent with {111} planes, the expected low-energy surface plane for HKUST-1. Following exposure to the moisture in ambient air—often even incidental exposure—particles develop mesoscale pores in 10 nm–1 µm range. The mesopores often follow linear paths, often along directions loosely consistent with nearby surfaces and apparent grain boundaries, and frequently have euhedral-looking edges. The commercial samples contain a greater diversity of external morphologies and internal mesopores, suggestive of greater intraparticle polycrystallinity. This suggests a link between polycrystallinity or coherent crystal defects and moisture-induced mesopore formation.

The images in a FIB/SEM dataset include contrast from anything in the line of site of the electron beam, not just the intended milling plane; for mesopores, this includes contrast from inside the pore. While this helped confirm that the pores were not caused by the beam (a real concern in many MOFs), it presents a unique challenge for image segmentation techniques. Supervised machine learning-based classification tools, such as WEKA, can be trained to recognize which features are beyond the milling plane, despite a lack of simple contrast indicators. A two-dimensional random forest model trained on planes artificially resliced perpendicular to the actual milling direction provided the best compromise between fidelity and computational cost was. Acceptable models usually required only a few training passes and ~10 features per class, with < 20 trees. Fully three-dimensional training yielded more visually compact pores, but the calculated volume percent difference between two and three dimensional classification were negligible.

FIB/SEM reconstructions can be used to measure the volume percent mesoporosity under nominally dry conditions, and after moisture exposure. Examples with up to ~30 vol% mesopore were found for casually-handled commercial HKUST-1 particles. 10–20 vol% mesopore was typical for lab-grown samples after ~1 day exposure to air. Internal mesopores would be easily missed by bulk diffraction techniques: the quality of diffraction might even improve as defective regions and grain boundaries are eroded. Likewise, the gravimetric capacity would overlook meso- to macroscale pores and voids in a microporous MOF. The volumetric capacities of MOFs tend to be significantly lower than predicted; for the case of HKUST-1, the formation of mesopores offers a simple explanation. Furthermore, understanding the three-dimensional structure informs better synthesis and handling strategies, whether to reduce the mesopore volume for storage applications, or to intentionally modulate mesoporosity for separations.

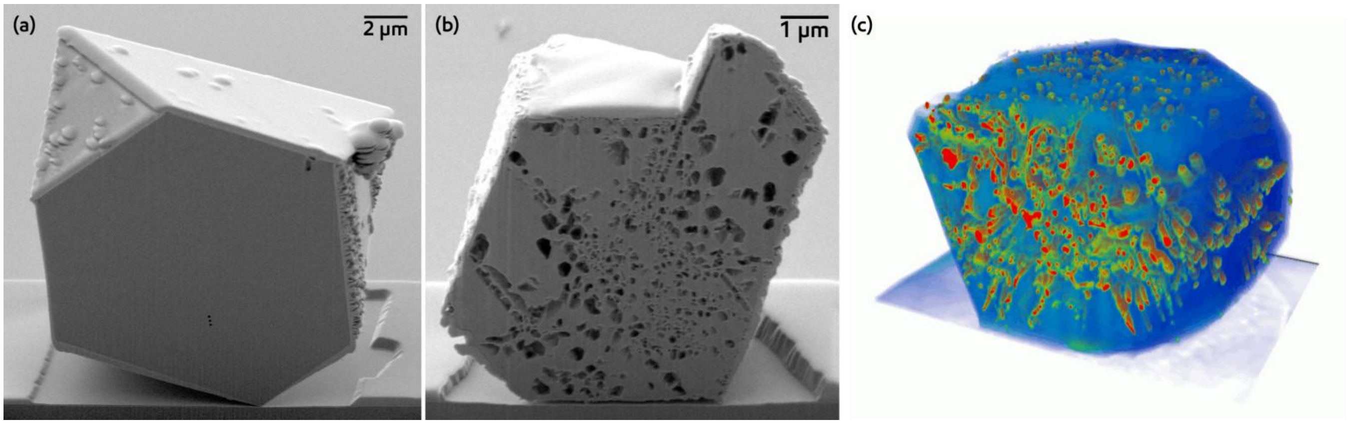

Figure 1. FIB/SEM sections of lab-grown HKUST-1 particles (85°C from water-ethanol solution) handled under dry conditions (a) as is, with minimal mesoporosity and (b) several days after brief exposure to ambient humidity air. There is a thick Pt/C coating deposited in situ. (c) A simple 3D rendering of a typical ~13-µm commercial HKUST-1 particle that has been exposed to air with >20 vol% resolved mesoporosity. The MOF has been left as a fairly opaque blue, as otherwise the mesopores are simply too dense for useful visualization.

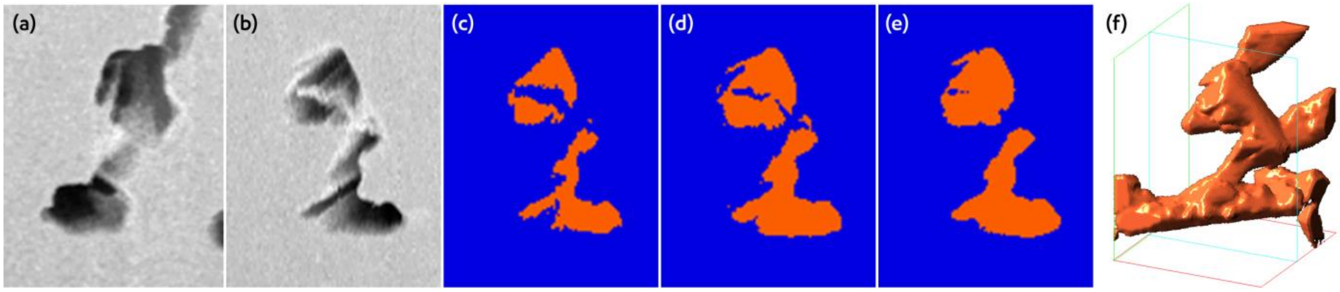

Figure 2. (a) A typical mesopore in HKUST-1 (lateral field of view is 1 µm). Features from the inside of the pore are visible in each image. (b) Visualizing an orthogonal section in the data, there is a clear directionality along the beam's viewing direct for features arising from inside the pores, as the same features are imaged in successive slices. (c) Segmentation by traditional methods confuses the inside of pores, but (d) two- and (e) three-dimensional supervised machine learning based classification can be trained to recognize the boundaries well (compared to manual segmentation). (f) Rendering the mesopore structure in this sub-volume of the MOF illustrates the nominally linear paths of many of the pores, and is suggestive of crystallographic orientations.

References
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