Metal-organic frameworks (MOFs) are a new class of porous materials, consisting of metal ion centers linked together by organic linkers to create crystalline porous networks. MOFs have received a great deal of attention because of their high specific surface areas and pore volumes, applicable in gas (H2) storage, catalysis, and photovoltaics.1 For specific applications MOF crystals can be loaded with catalytically active materials like Pd, Au, Cu and Ru in the form of nanoparticles, small clusters or single atoms, leading to a heightened activity in e.g. olefin hydrogenolysis and methanol synthesis or with semiconductor nanomaterials like GaN or ZnO for improved optical properties.2

Characterizing these delicate materials is far from trivial. Most of the common characterization techniques like X-ray diffraction of nitrogen adsorption for this type of materials offer global information only. However, in the case of nanostructured and/or -sized systems or upon loading of the frameworks, local structure information is of pivotal importance. Transmission electron microscopy is ideally suited for this, as it can provide structural information down to atomic resolution. MOFs can however be considered as soft matter and are therefore very sensitive to electron beam illumination, making TEM investigation of MOFs challenging.

One of the first MOFs studied by TEM was MIL-101 (Cr). The relatively stable nature of this MOF made pore imaging by HRTEM feasible3 Most other commonly-used MOF materials are significantly less stable to electron beam illumination. Improved TEM technology including low-voltage techniques, cooling holders, beam-blanking systems and fast-readout cameras however do allow pore imaging of far less stable MOFs like MOF-5 and ZIF-8.4 Advanced TEM techniques like tomography make it possible to determine the distribution of nanoparticles within the MOF framework, as in the recent example of hydrogen storage material Pd@COF-102.5 Combining imaging with spectroscopy in the electron microscope allows distinguishing between chemical species within the frameworks and measuring bonding at the local scale.1

Studying porous materials in 3 dimensions at the atomic scale is even more challenging. Again, beam damage is the limiting factor. We applied low-dose aberration corrected HAADF-STEM to zeolite crystals loaded with Ag. A careful analysis of HAADF-STEM images acquired along different zone-axes enabled us to propose a 3D model for the positions of the Ag ions.1

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Fig. 1: a) High resolution image of an intact cubic MOF-5 crystal (FT inset). 4 b) Enlarged image of region in the white box in a) with image simulation. c) Fourier filtered image with image simulation d) Simulated HRTEM image e) Structure of MOF-5; the white stripes in d) correspond to the terephthalate linkers of MOF-5, the pores are in grey.

Fig. 2: a) Tomographic reconstruction of Pd@COF-102. The Pd nanoparticles are rendered in gold, the COF framework in soft off-white. b) Orthoslice through the 3D reconstruction of a loaded Pd@COF-102. The particles visible as white dots are clearly present in the whole crystals without any preferential distribution in size or position.