Defect domain microstructure in UiO-66(Hf) revealed by scanning electron diffraction

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Defects in MOFs have a pronounced effect on their functional properties, modifying their porosity, mechanical properties, and catalytic activity. The UiO-66 class of MOFs exhibit a variety of defects arising from missing linkers as well as missing metal clusters. Missing cluster defects have been shown to form nanoscale correlated domains detectable in X-ray diffraction due to the modification of the crystal symmetry and topology from fcu in the pristine MOF to reo in the defect phase [1]. These defects have also been imaged at sub-nanometre spatial resolution by high resolution transmission electron microscopy [2]. However, the domain microstructure on the 50-100 nm length scale has not been recovered.

Scanning electron diffraction (SED), a type of four-dimensional scanning transmission electron microscopy (4D-STEM) in which two-dimensional diffraction patterns are acquired using a nanoscale electron beam rastered across a sample, has now revealed the shape, size, and crystallographic relationships of defect domains in UiO-66(Hf) prepared using formic acid modulated synthesis. Diffraction data were recorded at the electron Physical Sciences Imaging Centre (Diamond Light Source, UK) using a Merlin-Medipix hybrid counting-type direct electron detector to minimize beam damage by acquiring data using ~5 e/Å². By using a small convergence semi-angle (ca. 1 mrad), virtual dark field scanning transmission electron micrographs (VDF-STEM) were reconstructed using reflections characteristic of the fcu and reo phases for a series of defect-engineered UiO-66(Hf) samples [3]. Results showing blocky domain formation (Figure 1) indicate defect clustering arises in a highly ordered, crystallographically directed mechanism. These findings provide key experimental constraints for models of defect clustering in MOFs.

Figure 1. a, Annular dark field STEM and b, overlaid VDF-STEM images for a defect-engineered UiO-66(Hf) truncated octahedral particle reconstructed from SED data. c, d Diffraction patterns from regions marked in a. The arrows mark the scattering angles used for VDF imaging in b.

References