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Meeting-report

MicroED-Informed 4D-STEM of MOFs for Carbon Capture

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Metal–organic frameworks (MOFs) are cage-like structures composed of metal ions linked together by organic ligands. The metals and linkers in a MOF can be altered based on the desired functionality and structure. The tunable and structurally diverse nature of these materials, coupled with their high porosity and surface areas, make them optimal candidates for gas storage and capture [1]. Amines appended onto the MOF increase its selectivity for CO_2 from air. In particular, diamine-appended Mg_2(dobpdc) (dobpdc^{4-} = 4,4′-dioxidobiphenyl-3,3′-dicarboxylate) has the highest gravimetric capacity used for CO_2 capture from air. Structural characterization via single-crystal X-ray diffraction (SC-XRD) performed on an analogous material, diamine-appended Zn_2(dobpdc), showed that CO_2 adsorption proceeded via a cooperative mechanism, where the gas inserts into the metal-N bonds. Given that the strength of the metal-amine bond informs the adsorption properties, it is imperative to understand the structure of the material of interest instead of its metal analogue. Attempts at structural characterization of diamine-appended Mg_2(dobpdc) have been so far unsuccessful because it has not been possible to grow large enough single crystals for X-ray diffraction [2].

Recently, protocols using transmission electron microscopy (TEM) to solve micro- and nanosized crystals have been developed in the community [3, 4, 5]. In microcrystal electron diffraction (MicroED), the crystal is rotated continuously during data collection and diffraction patterns are collected as a movie by a fast camera [6]. In this study, MicroED was employed to solve the structure of several variants of diamine-appended Mg_2(dobpdc). This information was then used in tandem with scanning nanodiffraction or "4D-STEM" [7] in a low electron dose mode [8] to visualize heterogeneity within a crystal as well as between different crystals. We suggest that this heterogeneity affects the performance of the MOF in terms of its ability to adsorb gas. This idea is explored by *in situ* activation of the framework during data collection, allowing for structural comparison of an ensemble of CO_2-dosed and activated, or "bare" frameworks. The combined workflow of MicroED and 4D-STEM allows us to understand many performance-related aspects of a previously inaccessible structure [9].

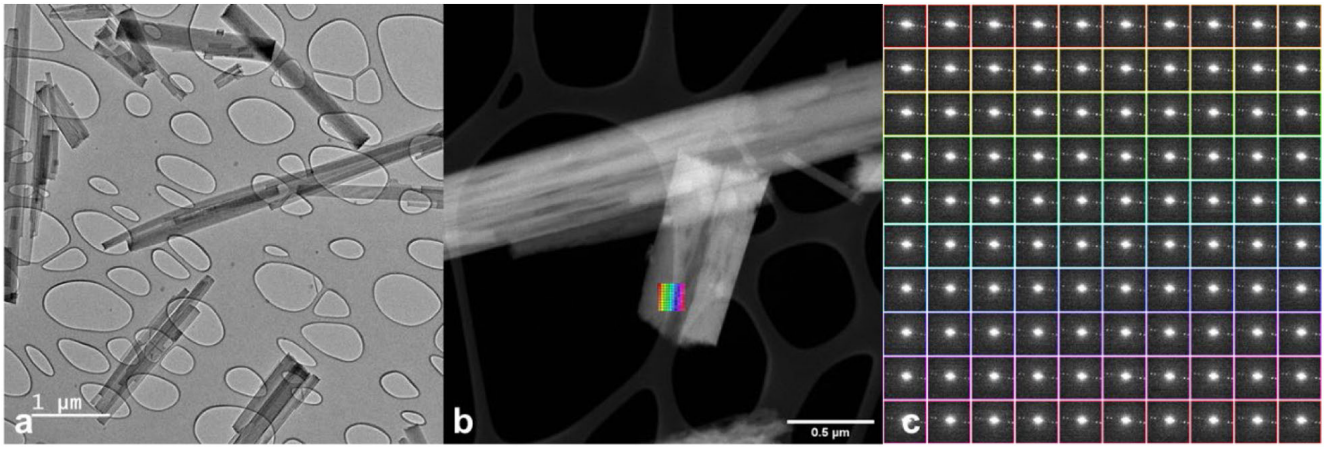

Fig. 1. (a) BFTEM (b) HAADF-STEM and (c) 4D-STEM of a 49x49 nm region (shown overlaid in color on b) of diamine-appended Mg_2(dobpdc). Although neighboring diffraction patterns (taken 4.9 nm apart) confirm that the crystal domain sizes are large enough for MicroED, mosaicity is present in the crystal.

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