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Electron Beam Damage Mechanisms in Solution Phase Electron Microscopy of Metal-Organic Frameworks

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Metal–organic frameworks (MOFs) are hybrid crystalline porous materials that have shown potential for a variety of applications, including gas storage, separation, catalysis, water capture, and drug delivery [1]. Liquid-cell electron microscopy (LCTEM) has shown potential to capture the nucleation and growth of MOFs in solvated conditions with unprecedented spatial and temporal resolution. However, MOFs are among the most beam-sensitive materials and can be easily damaged after exposure to a few electrons [2]. Therefore, there are only limited LCTEM studies on MOFs, focusing on a handful of MOFs. The prediction of the electron beam sensitivity of solvated MOFs and MOF monomers (metal ions, organic ligands, modulators) is a challenging task since multiple variables including size, orientation, guest molecules, geometry of ligand molecules, and microscope imaging conditions needs to be considered. In this work, we aim to identify the key parameters that influence the electron beam sensitivity of solvated MOFs, when exposed to the electron beam and under given operating conditions.

We directly visualize the radiolytic effects in solvated zeolitic imidazolate frameworks (ZIF) and 1,3,5-benzenetricarboxylate frameworks (BTC) under various solvent and imaging conditions to understand the electron-MOF-solvent interactions. The cumulative dose threshold that a MOF can withstand before being completely damaged is determined by *in situ* monitoring the size reduction and disappearance of MOFs in real-time. We observed that MOFs dispersed in alcohols are relatively stable compared to MOFs dispersed in water (**Figure 1**). We further identified that *in situ* damage of solvated MOFs is predominantly controlled by the solvent volume in the irradiated region, such that solvent radiolysis dominates other influencing factors – MOF particle size, aspect ratio, geometry of ligand molecules, solvent type, dose, flux.

In combination with four-dimensional scanning transmission electron microscopy (4DSTEM) [3], we demonstrate a *post-mortem* analysis to verify, and evaluate the extend of electron beam sensitivity in solvated MOFs *in-situ*. 4DSTEM experiments were performed using a JEOL ARM300 equipped with a Gatan K3-IS direct-electron detector operating at ~ 1140 frames per second. The electron beam energy was 300 keV, probe convergence angle was set to 1.6 mrad and, camera length of 200 mm. To cover the large field of view of 3.56 µm × 3.56 µm, a scan step size of 18 nm was used. Electron total dose per dataset was set to <100 e^-, to keep beam-induced damage to a minimum. Areas of the *post-mortem* sample were analyzed to evaluate the degree of crystallinity and angular distribution. An example of this analysis is shown in **Figure 2**. To have a full picture of the MOF distribution, a virtual dark-field image (**Figure 2A**) was obtained by using a virtual aperture applied to scattering angles higher than 20 mrad in the reciprocal space (see inset in **Figure 2A**). Local investigation of distinguished areas within the field of view (**Figure 2B, Figure 2C**) shows reminiscent ZIF-8 crystallites at different orientation in relation to the incident electron beam. We can use the diffraction patterns obtained at each pixel to generate orientation maps as shown in **Figure 2D**. Such maps can help us to distinguish areas where MOF sustained the crystallinity and their angular distribution. At last, this study identifies the key parameters that influence the electron beam sensitivity in MOFs grown in situ, and further demonstrates the use of 4DSTEM as a *post-mortem* method to characterize the MOFs observed *in situ* [4].

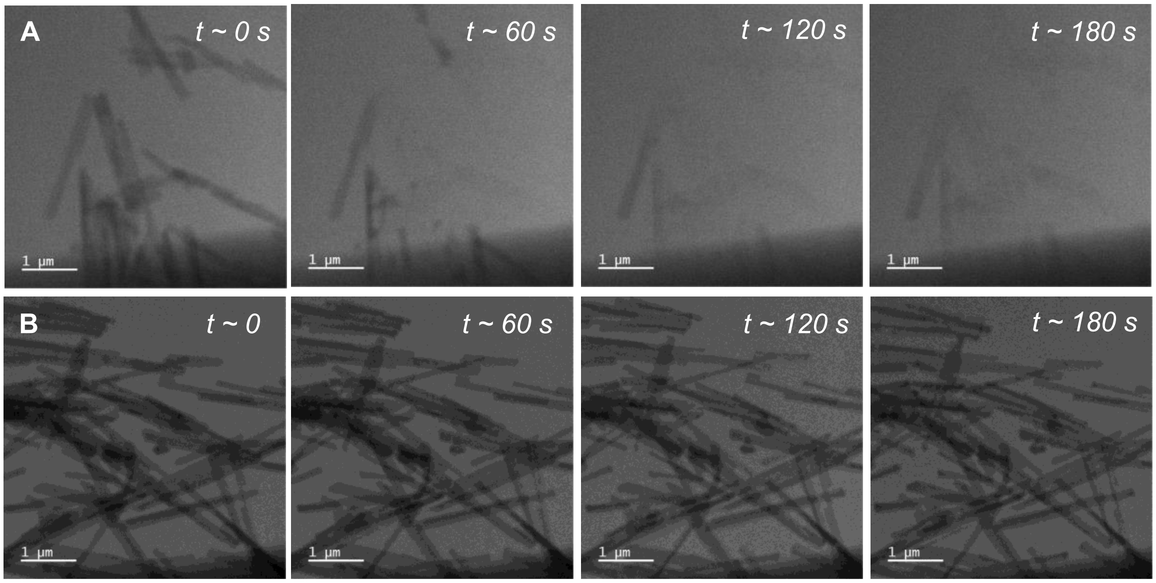

Figure 1: Time lapse LCTEM snapshots of Eu-BTC MOFs dispersed in water (A) and ethanol (B). Solvent radiolysis and subsequent damage to MOFs is more pronounced in water compared to ethanol.

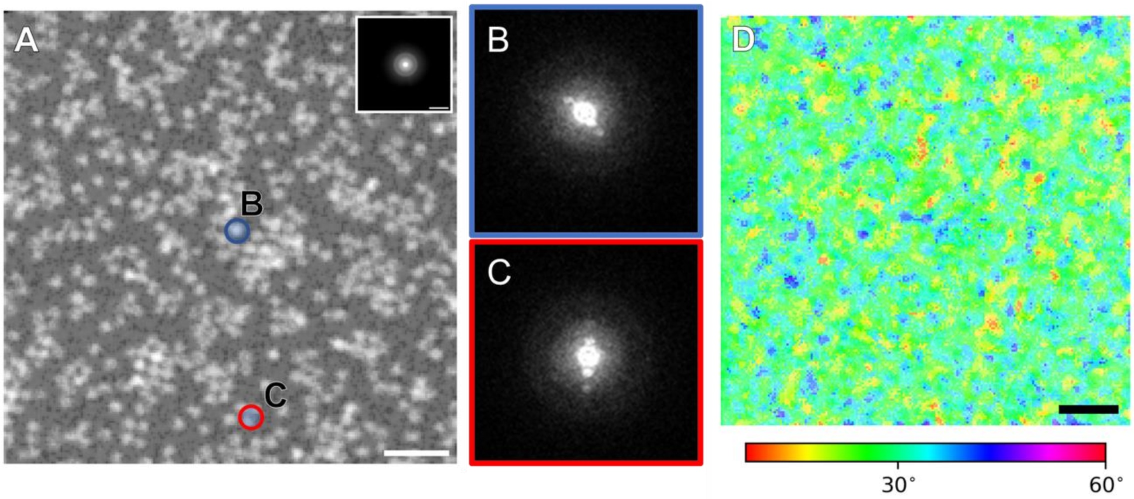

Figure 2: *Post-mortem* analysis using 4DSTEM. (A) Shows a ADF image retrieved by integrating the reciprocal space (inset). In the field of view, we can observe ZIF-8 MOF crystallites oriented differently in the diffraction pattern obtained from the areas marked as B and C. (D) Orientation map generated using the local information from diffraction patterns. Scale bars are 500nm.

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