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Understanding Structural and Chemical Modifications of ZIF MOF Under Electron-Beam Irradiation using STEM-EELS

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Zeolitic imidazole frameworks (ZIFs) are a type of metal organic framework (MOF), where Zn metal atoms are tetrahedrally coordinated to imidazole linkers [1]. ZIFs are widely studied as potential materials of interest in electronic devices and sensor applications due to their low-dielectric constants [2]. For device applications, high precision patterning of the ZIFs is essential, which has been demonstrated by using an electron [3] and X-ray beam [4]. To optimize these patterning techniques, it is necessary to understand the structural and chemical changes happening in the MOF framework upon electron-beam irradiation. This has been widely studied in other inorganic crystalline materials like zeolites [5], but is limited for MOFs. Here, we study the transition of a ZIF-L MOF from an ordered crystalline state to a disordered amorphous state using dose-controlled transmission electron microscopy (TEM) coupled with electron energy-loss spectroscopy (EELS) to simultaneously monitor chemical changes during the transition [6].

First, structural changes in ZIF-L were monitored using dose-dependent electron diffraction. It was observed that at an accumulated dose of ~ 100 e/Å^2, there is a complete loss in diffraction intensity along with the appearance of broad amorphous like peaks indicating the formation of an amorphous ZIF-L phase. Further, shifts in diffraction peaks with dose indicates a decrease in the lattice parameters, which is also observed as particle shrinkage in the high-angle annular dark-field scanning TEM (HAADF-STEM) images. Thus, in the initial stages of beam exposure, it can be concluded that there is a collapse of the porous framework resulting in the formation of a "disordered" amorphous ZIF-L phase, retaining the short-range order of the parent framework. These changes are summarized in Figure 1.

To study the chemical changes ZIF-L during this transformation, core-level EELS spectra were obtained from C, N and Zn as a function of dose to monitor changes in the fine-structure which are sensitive to the local chemical environment. EELS spectra were collected on an aberration corrected FEI Titan G2 60-300 (S)TEM microscope on an Enfinium ER spectrometer. The microscope was operated at 200 keV with a probe current of 10 pA. At doses < 100 e/Å^2, changes in the fine-structure were minor indicating no changes in the local bonding of the amorphous ZIF-L (Fig. 2(a)). At higher doses > 500 e/Å^2, considerable changes were observed in the core-level EELS fine-structure, resulting from the radiolytic modification of the imidazole linkers by the loss of methyl groups and ring opening reactions, degrading the linker in the second stage of the structural modification. These results point to a completely radiolytic behavior of the electron-beam-ZIF interaction (Fig. 2(b)). Thus, changes in the ZIF MOF occur in two stages, wherein first amorphization occurs followed by linker damage (Fig. 2(c)). Further, these structural modifications impact the dielectric properties of the material by shifting the energy for the optical transitions, which is important for device applications [7].

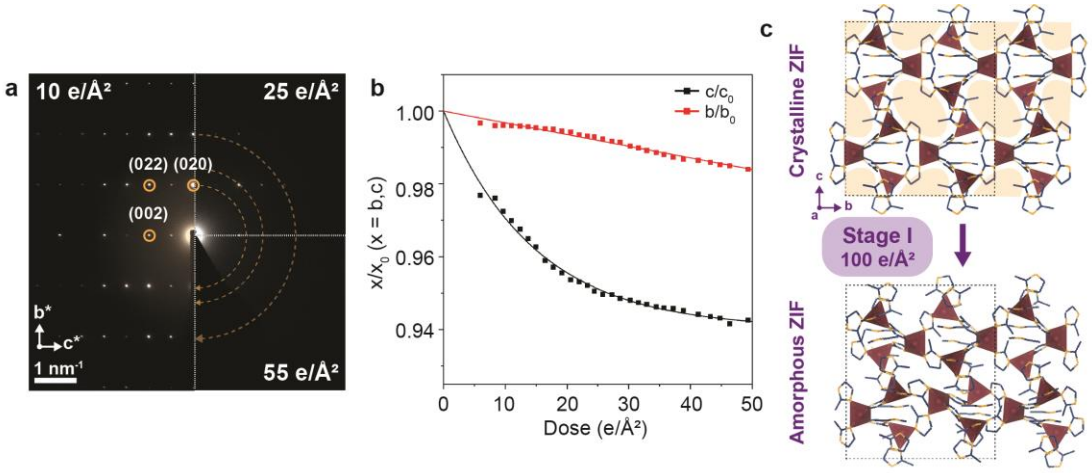

Figure 1. (a) Electron diffraction from crystalline ZIF MOF, showing loss in intensity as a function of dose. (b) Changes in lattice parameters along the *b*- and *c*-directions. MOF particles lay on the TEM grid with their *a*-direction parallel to the incident beam. (c) The structural changes are summarized using the unit-cell model of the ZIF MOF.

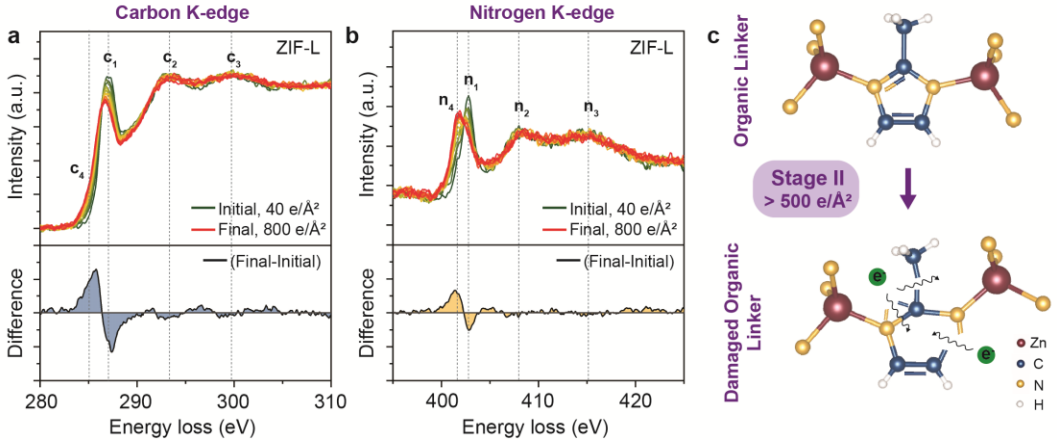

Figure 2. (a, b) Core-level spectra for the C and N K-edges respectively collected from a ZIF-L particle as a function of dose. To visualize the changes, difference spectra is shown in the panel below. (c) Modifications correspond to the changes occurring in the organic linker molecule resulting from radiolytic damage.

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