

Electron-Beam-Damage in Metal Organic Frameworks in the TEM

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Metal Organic Frameworks (MOFs) are hybrid inorganic-organic porous materials that are gaining interest for applications in catalysis, gas-storage, and gas-separations [1]. The visualization of the atomic structure of MOFs is necessary to study their crystal structure, interfaces and defects in them to understand the mass-transport and sorption characteristics [2]. Investigation of the MOF atomic structure in the TEM is challenging due to unusually high electron beam-sensitivity of the material [3]. A systematic study of the electron-beam-damage mechanisms occurring in MOFs is needed to enable characterization of MOFs in the TEM. Damage in the TEM occurs due to inelastic scattering of probe electrons with the atoms of the sample, leading to knock-on damage, radiolysis and charging in the specimen [4]. In this study, we examine one of the common MOFs, Zeolitic Imidazolate Framework, ZIF-8, to understand the dominating damage mechanism and evaluate the damage cross-sections for radiolysis (σ_r) and knock-on (σ_k). The results will be compared to the damage mechanisms in zeolites, which are also porous beam-sensitive materials [5].

ZIF-8 was synthesized in an aqueous system using $Zn(NO_3)_2 \cdot 6H_2O$ as the source for the metal and 2-methylimidazole as the organic linker [6]. Electron diffraction was performed in FEI Technai G² F30 (S)TEM equipped with a Schottky FEG and operated at 300 kV. Diffraction patterns were acquired from the nanoparticles at three dose-rates: 2.91, 1.14 and 0.34 e/Å²s (Figure 1a). The diffraction patterns were radially averaged for better statistics and a power-law background subtraction was performed to extract the intensities corresponding to the planes. The diffraction intensities were analyzed to obtain the characteristic doses (D_c) for the damage, which is indicated by 50% reduction in the initial-intensity of the (011) diffraction spots (Figure 1b).

The damage cross-sections obtained for ZIF-8 were then compared with those obtained for MFI zeolite. The threshold values for knock-on damage for Zn and N atoms were calculated by using the Zn-Imidazole binding energy of 2.15 eV/bond [8]. The results show that knock-on damage should be present at most beam voltages used in typical TEMs. However, we find that radiolysis appears to be the dominating mechanism for damage at 300 kV for MOFs, whereas for MFI, both knock-on damage and radiolysis are active at these energies [9].

References:

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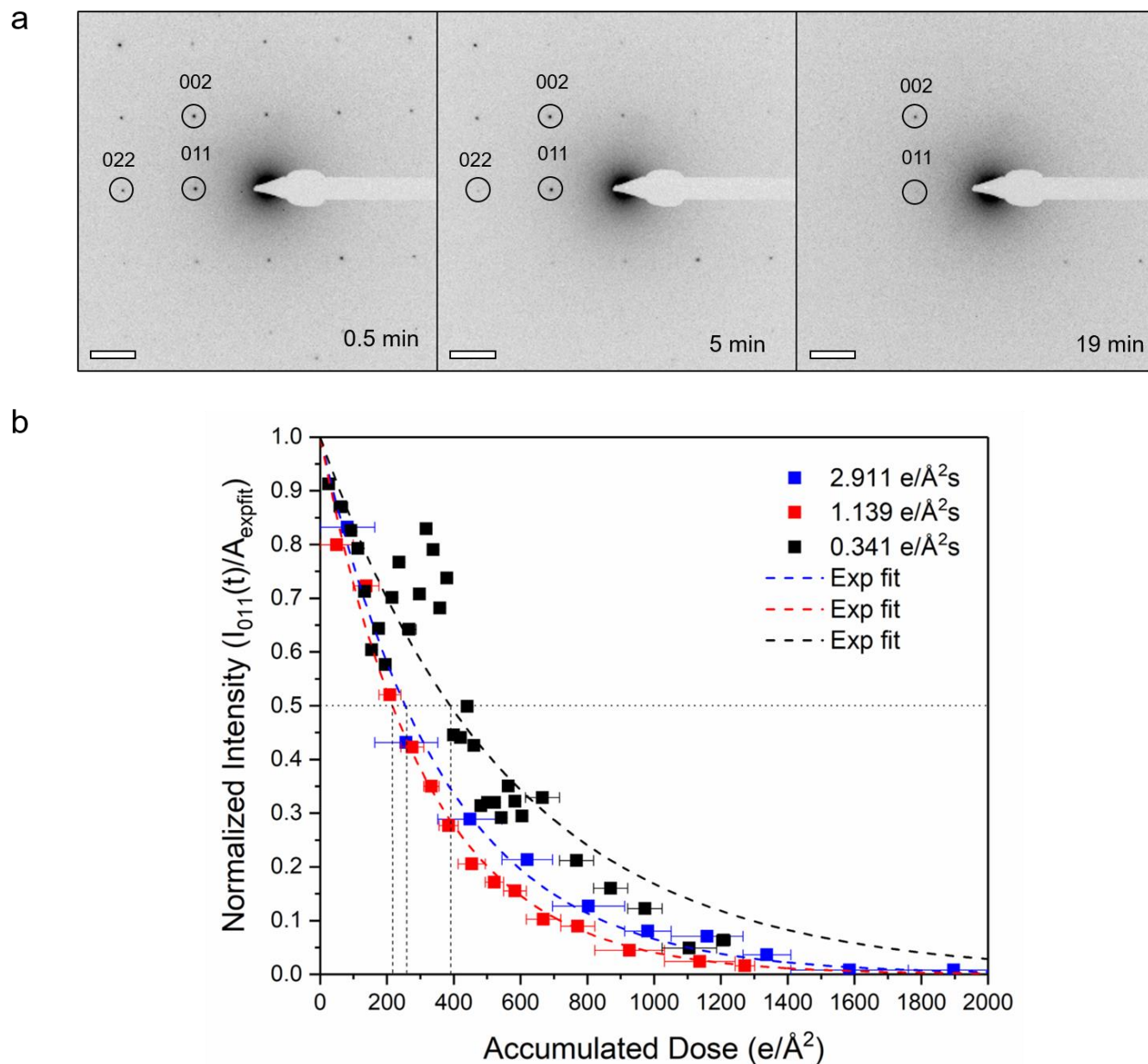


Figure 1: (a) Electron Diffraction collected from a ZIF-8 nanocrystal at beam energy 300 kV and dose rate $0.34 \text{ e}/\text{\AA}^2$, scale bar is 0.5 nm^{-1} ; (b) Normalized background subtracted intensities for the (011) spot for the three dose-rates with indicated critical doses (D_c).