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Vibrational Spectroscopy of Beam-Sensitive Materials in the Transmission Electron Microscope

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Most materials undergo some damage when exposed to a high energy electron beam. This can be especially challenging for the study of organic functional materials that are of increasing interest due to novel magnetic or electronic properties [1]. One of the most beam-sensitive groups of materials are the metal-organic frameworks (MOFs). MOFs are a type of network expanded structure, where metal cation clusters are connected by organic linking molecules. These materials have been proposed for numerous applications from biomedical treatments to nuclear remediation efforts, and, with a greater understanding of their fundamental properties, MOFs may be used in even more applications to continue advancing society[2].

Understanding the bonding and local properties are of particular interest in obtaining a more fundamental knowledge of these materials. While vibrational spectroscopy can be a powerful tool to analyze the bonding of novel materials, methods such as Raman and Infra-red spectroscopies have very limited spatial resolution and provide relatively delocalized information about the sample. The natural evolution of vibrational spectroscopy is to use the flexibility and resolution of scanning transmission electron microscopy to collect localized vibrational data[3]. Recently, more sensitive detectors, better spectrometers, and brighter electron sources have allowed vibrational spectroscopy to be performed in the electron microscope. Previous work has established that, with careful setup of acquisition parameters, vibrational spectroscopy can be performed with near-atomic scale spatial resolution[4]. Vibrational losses are typically on the order of millielectron-volts, and only recently have instruments sufficiently high energy resolution to detect them been developed[5]. The cross-section for vibrational losses detected using electron energy-loss spectroscopy (EELS) in the STEM is relatively small, which makes the study of beam sensitive materials especially challenging. In this contribution we will discuss our initial efforts to use STEM-EELS to probe inelastic losses in copper ruthenium oxalate MOF (Fig. 1). Initial sample preparation by liquid exfoliation has enabled the formation of thin samples suitable for STEM-EELS. (Fig. 2) We will discuss the potential of low dose imaging, smart acquisition routines and cryogenic sample stages to create a feasible environment to collect vibrational data on MOFs in the microscope.

$$(NBu_4)[Cu^{II}Ru^{III}(C_2O_4)_3]$$

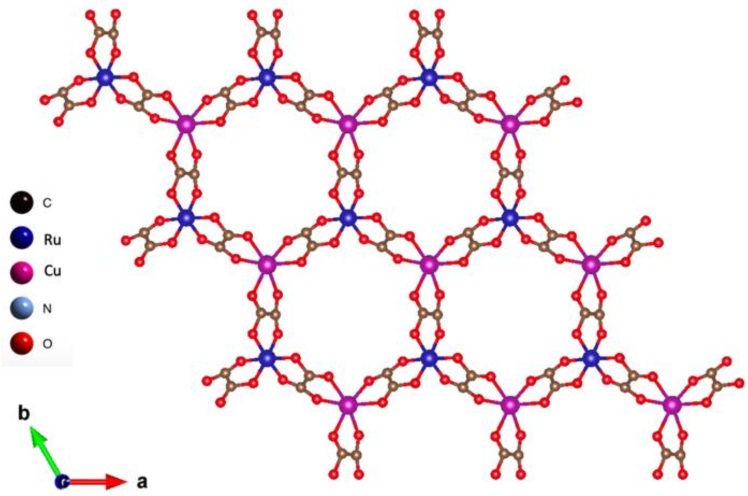

Figure 1. The chemical structure of a copper ruthenium oxalate MOF

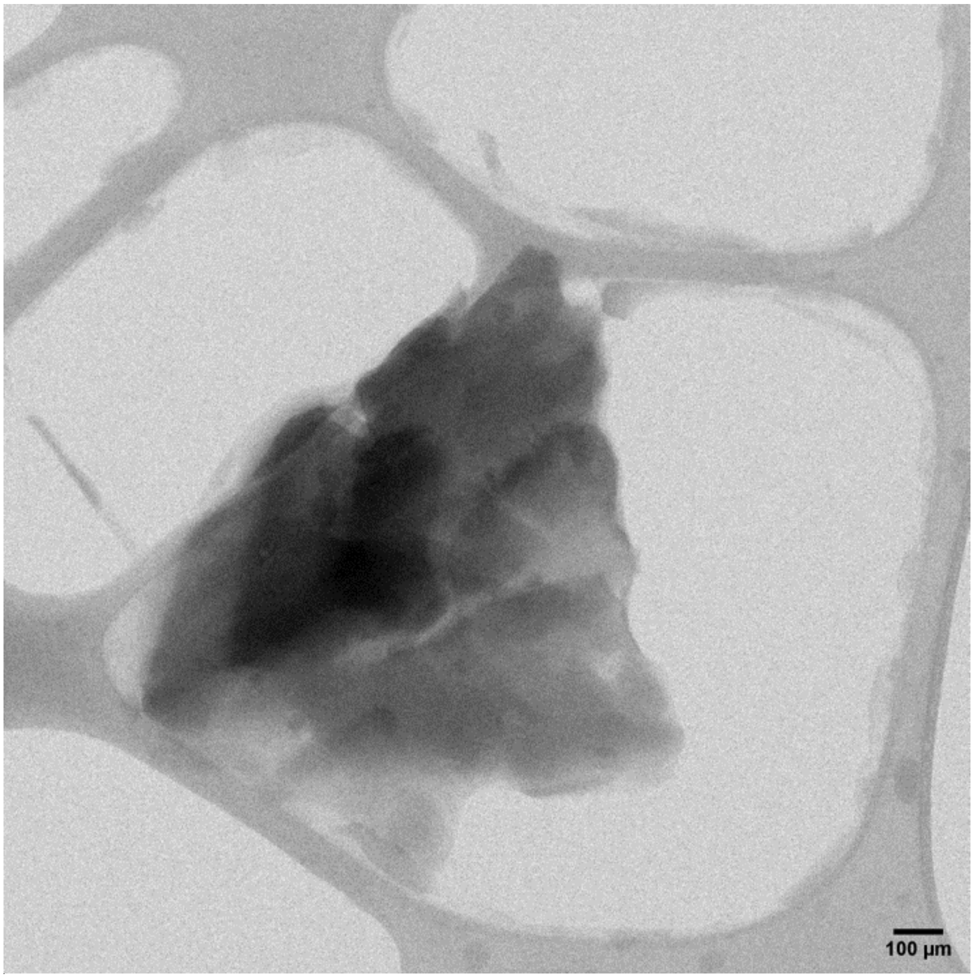

Figure 2. A transmission electron micrograph of an MOF flake produced by ultrasonic exfoliation in absolute ethanol.

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