

# Tuesday Afternoon Poster Sessions

## In Situ Microscopy and Spectroscopy Focus Topic

Room: Central Hall - Session IS-TuP

## In Situ Microscopy and Spectroscopy Poster Session

**IS-TuP2 *In Situ* Infrared Spectroscopic Studies of the Stability of Nanoporous Materials in Water Vapor for Gas Adsorption and Separation.** K. Tan, N. Nijem, The University of Texas at Dallas, P. Canepa, Wake Forest University, Q. Gong, J. Li, Rutgers University, T. Thonhauser, Wake Forest University, Y.J. Chabal, The University of Texas at Dallas

The stability of nanoporous metal organic frameworks (MOFs) materials in water vapor is a critical issue that must be taken into account for its potential industrial applications such as energy carrier gases (H<sub>2</sub>, CH<sub>4</sub>) storage, greenhouse gas CO<sub>2</sub> capture. Many previously reported MOFs structures decompose upon exposure to air, which results in a reduced gas uptake and limits their large scale application. In this context, the study of the interaction and possible reaction of water with MOFs is extremely important to obtain insight into the mechanism of MOFs dissociation in humid environments. In our study, the hydration process of prototypical MOFs M(bdc)(ted)<sub>0.5</sub> [M=Cu, Zn, Ni, Co; bdc= 1,4-benzenedicarboxylic acid; ted= triethylenediamine] by water vapor was monitored by *in situ* infrared spectroscopy as a function of pressure and temperature. Infrared spectroscopic results from M(bdc)(ted)<sub>0.5</sub> compounds indicate that the condensation of water vapors into the framework is necessary to initiate the dissociation reaction of the metal-ligand bond; the stability or modification of M(bdc)(ted)<sub>0.5</sub>-compound structure upon exposure to water vapor critically depends on the central metal ions. Combining with results taken by *ex situ* Raman spectroscopy and X ray diffraction, we conclude that the hydrolysis reaction of water molecules with Cu-O-C group induces the Cu(bdc)(ted)<sub>0.5</sub> structure decomposition; for Zn(bdc)(ted)<sub>0.5</sub>, Co(bdc)(ted)<sub>0.5</sub>, the water molecules replace ted pillars and bond to the apical sites of the paddle wheel building units of Zn<sub>2</sub>(COO)<sub>4</sub> and Co<sub>2</sub>(COO)<sub>4</sub> by oxygen atoms; Ni(bdc)(ted)<sub>0.5</sub> is less susceptible to reaction with water vapors than the other three compounds under the same conditions. These experimental conclusions are well supported by first principles theoretical van der Waals density functional (vdW-DF) calculations of overall reaction enthalpies. This work constitutes the first systematic investigation of the decomposition mechanism of isostructural MOFs with different central metal ions in the presence of moisture. The findings within this work make it possible to determine the operating conditions of this class of MOFs with paddle wheel secondary building units and provide guidance for developing more robust units.

**IS-TuP3 Determination of the Mechanisms of Photooxidation of CdSe/ZnS Quantum Dots/Shells.** L.J. Powell, S. Saurabh, M. Bruchez, Carnegie Mellon University, L.F. Allard, Oak Ridge National Laboratory, L. Qu, M. Bootman, Crystalplex Inc., R.F. Davis, Carnegie Mellon University

Realization of the potential of Quantum Dots (QDs) for biological, energy-efficient lighting and energy harvesting applications requires that their long-term photostability be improved, especially with regards to protection from photooxidation. The overarching objective of this project is the determination of the chemical and physical mechanisms of photooxidation of CdSe QDs. Pittsburgh-based Crystalplex, Inc. is providing 5 nm CdSe QDs for this research. Three integrated *in situ* characterization techniques are being used to observe changes in QD morphology, optical behavior, and surface chemistry during photooxidation conditions. We are conducting novel microstructural *in situ* experiments in an aberration-corrected STEM/TEM using a Protochips environmental chamber. Changes in the morphology of single QDs are observed in real-time under O<sub>2</sub> and N<sub>2</sub> atmospheres up to 1 atm while maintaining atomic resolution. Multiple series of digital micrographs and EDX data are shown. Single-molecule fluorescence microscopy experiments are allowing us to observe real-time changes in the photoluminescence (PL) behavior of single QDs. The QDs are exposed to 1 atm of either pure O<sub>2</sub> or an inert gas in an environmental chamber and excited with a 490 nm light source during measurements. Changes in blinking rates and PL intensities are analyzed with respect to the periods of exposure to O<sub>2</sub> and light. A series of images and associated statistical analysis are discussed in this poster. *In situ* XPS at CMU is being used to identify the chemical and bonding states of the reacting species. Analysis of the acquired spectra is also presented. These complementary *in situ* experiments allow us to assemble a description of the step-by-step photooxidation mechanism.

**IS-TuP4 Coherent X-ray Imaging.** T. Senkbeil, T. Gorniak, A. Buck, Karlsruhe Institute of Technology, Germany, K. Giewekemeyer, T. Salditt, University of Goettingen, Germany, A. Rosenhahn, Karlsruhe Institute of Technology, Germany

X-ray microscopy of hydrated biological samples – especially in the so-called water window of 284-540 eV – is of tremendous interest for life sciences due to the high intrinsic contrast of organic matter with respect to the aqueous background and the higher penetration depth compared to transmission electron microscopy. We present X-ray microscopy of cryogenic samples using the coherence-based imaging technique called ptychography.

Ptychography combines previous coherent X-ray diffraction imaging (CXDI) approaches with a scanning scheme, thus providing the ability to image bigger samples, like whole cells or bacteria. We have performed soft X-ray ptychography experiments using our dedicated vacuum chamber HORST at different soft X-ray beamlines at the synchrotron source BESSY II in Berlin, demonstrating chemical contrast and resolutions down to 50 nm in test samples. After upgrading our vacuum chamber with a cryo-sample stage, we now present first results of soft x-ray ptychography of cryogenic samples. Cryo-fixation preserves the natural hydrated state of biological specimens and eliminates the need for any further preparation step, which might possibly alter the ultra-structure. By keeping the sample at temperatures around 120 K at all times, recrystallization of the amorphous water is avoided and the effects of radiation damage during the scans are minimized.

# Authors Index

**Bold page numbers indicate the presenter**

— **A** —

Allard, L.F.: IS-TuP3, 1

— **B** —

Bootman, M.: IS-TuP3, 1

Bruchez, M.: IS-TuP3, 1

Buck, A.: IS-TuP4, 1

— **C** —

Canepa, P.: IS-TuP2, 1

Chabal, Y.J.: IS-TuP2, 1

— **D** —

Davis, R.F.: IS-TuP3, 1

— **G** —

Giewekemeyer, K.: IS-TuP4, 1

Gong, Q.: IS-TuP2, 1

Gorniak, T.: IS-TuP4, 1

— **L** —

Li, J.: IS-TuP2, 1

— **N** —

Nijem, N.: IS-TuP2, 1

— **P** —

Powell, L.J.: IS-TuP3, **1**

— **Q** —

Qu, L.: IS-TuP3, 1

— **R** —

Rosenhahn, A.: IS-TuP4, 1

— **S** —

Salditt, T.: IS-TuP4, 1

Saurabh, S.: IS-TuP3, 1

Senkbeil, T.: IS-TuP4, **1**

— **T** —

Tan, K.: IS-TuP2, **1**

Thonhauser, T.: IS-TuP2, 1