



Probing the crystal phase transformation in plasmonic copper sulfide nanocrystals during electrochemical experiments (26-01-1125)

Experimental report for experiment 195.068.1041

Ward van der Stam

**Experiment date and duration:** November 27, 2017, until December 1, 2017, 9 shifts

**People present during the experiment:** Ward van der Stam, Jaco Geuchies, Nick Kirkwood, and Solrun Gudjonsdottir

**Local contact:** Alessandro Longo

## Overall assessment of the experiment

During the allocated time the beamline performed very well. We had no issues with the beam or the detectors, so all the planned experiments could be carried out. Therefore, we could use all the available beamtime to acquire data without being troubled by side issues.

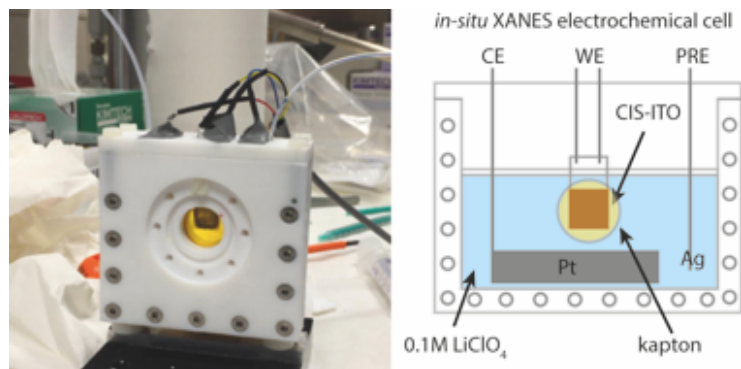
The only issue we encountered, was that the top-up mode of the ring created fluctuations in our signal. Therefore, we had to acquire many short scans, instead of longer averaged scans, and we could not measure the EXAFS region. Despite these issues, we acquired a large dataset. At the moment we are processing and analyzing the data and we believe to be able to draw valuable conclusions soon. One part of the dataset is already included in a manuscript, which is currently under review at ACS Nano.

## Experimental set-up

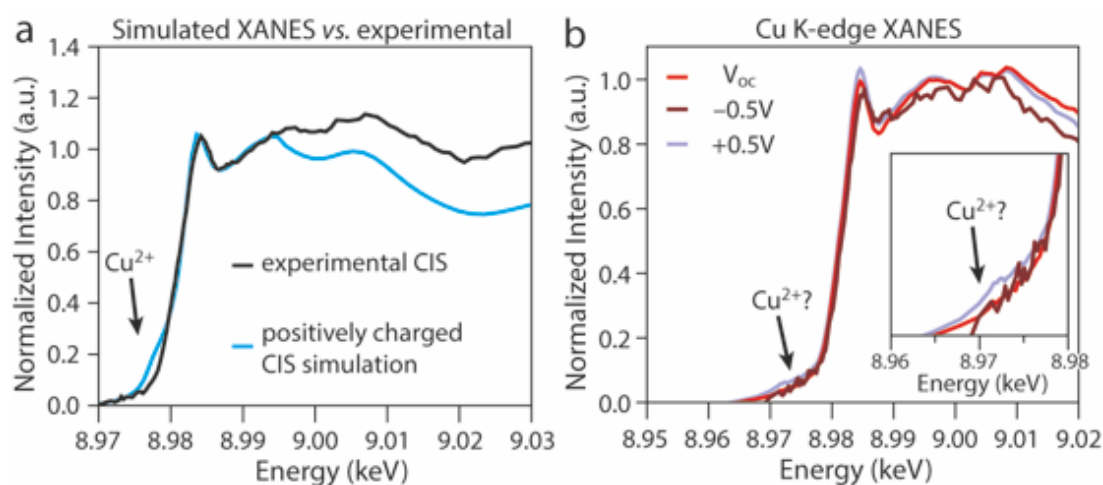
Our electrochemical cell (Figure 1) was designed for transmission mode, but during the course of the experiments we found out that fluorescence mode would be beneficial for the signal to noise ratio of the acquired XANES spectra. Another drawback of our electrochemical cell design was that the exit angles for the diffracted X-ray was too small to get reasonable results for the *in-situ* XRD. The cell design should be optimized in the future in order to measure the XANES and XRD simultaneously.

## Preliminary results

In our experiments, CuS particles are lithiated and delithiated by the application of an external potential with respect to the Ag pseudoreference electrode. This causes sulfur-sulfur bonds within the nanoparticles to be reduced, upon which  $\text{Li}^+$  intercalates into the material to ensure charge balance. We found indirect evidence for  $\text{Li}^+$  intercalation by our electrochemical measurements, but we intended to verify this with *in-situ* XANES. We found preliminary evidence in our analysis that  $\text{Li}^+$  indeed intercalates into the CuS nanoparticles, but more detailed analysis is needed. Furthermore, we performed test experiments on a different set of nanoparticles, in which we intended to probe the oxidation state of the Cu cations in  $\text{CuInS}_2$  nanoparticles. These tentative results have been incorporated in a manuscript that is currently under review at ACS Nano. These measurements indicate that there are small variations in the chemical environment of the Cu cations, but it is inconclusive at this point whether it is the oxidation state or the coordination sphere that changes upon oxidation (Figure 2).



**Figure 1.** Picture of the *in-situ* X-ray absorption near-edge spectroscopy (XANES) electrochemical cell (left) and schematic representation (right).



**Figure 2.** (a) To understand the observed features better, the XANES patterns were simulated together with the local contact, Alessandro Longo, which indicate a pre-edge feature related to  $\text{Cu}^{2+}$ . (b) Preliminary XANES analysis of the spectra obtained for  $\text{CuInS}_2$  nanocrystals at different applied potentials. Small variations can be observed at the Cu K-edge. The pre-edge feature related to  $\text{Cu}^{2+}$  is also slightly observable in the experimental patterns at oxidizing potentials.

## Conclusions and Outlook

We will be able to draw important conclusions about the intercalation of  $\text{Li}^+$  in copper sulfide and the coordination sphere of Cu cations in  $\text{CuInS}_2$  nanoparticles. Some technical issues related to the electrochemical cell and the signal-to-noise ratio should be optimized in order to draw clear conclusions, but the preliminary results already look promising.