ESRF	**Experiment title: In-situ photon-in photon-out spectroscopy measurements on ultra-small Cu3N nanoparticles**	**Experiment number**: HC4929
Beamline: ID26	**Date of experiment**: From: 01.03.2022 to: 07.03.2022	**Date of report**:
Shifts: 18	**Local contact(s)**: Jan Pieter Glatzel	*Received at ESRF:*

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Report:

We measured the in-situ Cu K-edge (8979 eV) HERFD-XANES and VtC XES during the controlled synthesis of ultra-small Cu_3N/Cu_3PdN colloidal nanoparticles in the first part of our beamtime. All the samples and precursor mixtures were prepared in the argon-filled glove bags at the main chemistry lab of the ESRF. Our sincere thanks to Dr Herald Muller for arranging the glove bags for our experiment. For each sample preparation, the glove bags were flushed with Ar for 5-10 times to ensure an inert environment. The reaction precursors such as $Cu(OCH_3)_2$ and C_7H_9N for Cu3N synthesis were added together in the PEEK capillary and placed in the in-situ reaction cell. In addition to the $Cu(OCH_3)_2$ and C_7H_9N, $Pd(acac)_2$ was added for the Cu_3PdN synthesis. The reaction cell is further sealed completely before removing from the glove bag. The precursor-filled reaction cell is brought to the beamline hutch and placed for the measurements. As explained in the proposal, the in-situ reaction cell is composed of a reaction chamber with low-power heating elements and a magnetic micro stirrer. The reaction cell is directly connected to the Lakeshore and the power supply to control the temperature. After the measurements, the samples were collected and brought back to our home institute for further studies.

Si(444) and Ge(800) analysing crystals were used. The measurements were extremely challenging because of the beam damage. The precursor was very sensitive to x-rays and when the x-ray is exposed to the sample for more than 50 s on the same spot, the copper methoxide complex is reduced to metallic and deposited on the walls of the PEEK capillary. Thus, we measured HERFD-XANES spectra at different spots (10 sec/spectrum and 4 spectra/spot). Under such conditions, the in-situ measurements were carried out from 25 °C to 140 °C with a ramp of 10 °C/min and stayed at 140 °C for 30 min. The preliminary understanding is the Cu (II) complex is directly reducing to Cu (I) nitride. Figure 1a shows the Cu K-edge in-situ HERFD XANES of Cu3N.

We also measured both XANES and VtC XES of CuO, Cu2O, Cu-foil, Cu(OCH3)2, Cu(acac)2 powder reference samples.

The VtC XES spectra were recorded as one data point/spot, taking around 50 min per spectrum. Thus, the VtC XES measurements took longer than the HERFD. We recorded VtC spectra at 20 °C, 40 °C, 60 °C, 80 °C, 100 °C, 120 °C and at 140 °C. The XES spectra have a poor quality even after being corrected with the concentration factor.

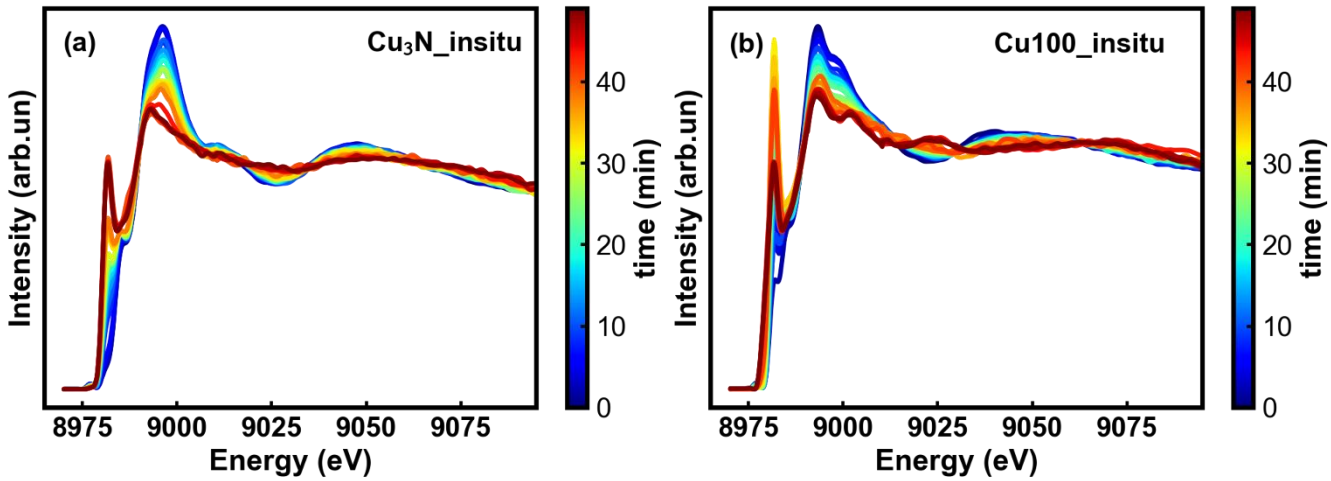

Figure 1. In-situ Cu K-edge HERFD-XANES of (a) Cu3N colloidal nanoparticles and (b) Cu^0 colloidal nanoparticles.

We then measured the in-situ HERFD-XANES during the colloidal synthesis of ultrasmall Cu nanoparticles and CuPd bimetallic nanoparticles. The reaction precursors $Cu(acac)_2$, $Pd(acac)_2$, co-reactants/stabilizers (Oleicacid, Oleic ammine, 1,2-Hexadecandiolo) and solvents (Benzyl alcohol, 1-Octadecene) were filled in the PEEK capillary and fixed and sealed properly in the reaction cell. The in-situ data were acquired from 25 °C to 220 °C with the ramp rate of 10 °C/min and stayed at 220 °C for 30 min. Figure 1b shows the in-situ HERFD XANES of Cu nanoparticles. The preliminary result shows that the Cu^{2+} is reduced to Cu^{1+} at around 210 °C and then to Cu^0 further increasing the temperature. The in-situ Cu K-edge HERFD-XANES of Cu100 is shown in Figure 1b. The detailed analysis is in progress and we will publish the results soon.