



Experiment title: In situ photon-in-photon-out spectroscopic studies with high temporal, spatial and energy resolution during emergence of transition metal sulfides and nitrides

Experiment number:
MA-5366

Beamline: ID24	Date of experiment: from: 03.05.2023 to: 09.05.2023	Date of report:
Shifts: 18	Local contact(s): Olivier Mathon	<i>Received at ESRF:</i>

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Report:

In the beginning, we set up the beamline to measure at the Zn K-edge HERFD-XANES. Si 642 analysing crystals were mounted and the beam spot size was 0.3 mm * 1 mm. We wanted to measure the in-situ HERFD-XANES during the synthesis of ZnS nanoparticles. The samples and the precursor mixtures were prepared at the chemistry lab in the experimental hall. The Zinc acetate, sulfur and oleylamine were mixed together in a glass vial and stirred until the salts dissolved completely. A 200 µl of clear precursor solution is added to the PEEK capillary and sealed completely in the reaction cell. Figure 1a shows the sketch of the in-situ reaction cell. It is composed of a reaction chamber with low-power heating elements, a temperature sensor and a magnetic micro stirrer. Then the reaction cell is directly mounted on the sample stage in the experimental hutch. Initially, We checked the sample damage due to the x-ray beam using different attenuation factors for a few hours and fixed the attenuation factor of 10 for further measurements. We ran the in-situ reaction from 25 °C to 180 °C at the ramp rate of 10 °C/min. and stayed at 180 °C for 120 min.

Then we checked our new microfluidic device which was developed by our group at CHyN, Hamburg. The microfluidic device is made of Si wafer with a microfluidic channel having an inlet and outlet tubes. The microfluidic channels are covered with borofloat glass on top. The tubes are connected using PDMS polymer. The inlet tubes are connected to the syringe containing the precursor solution and the syringe is connected to the pump to control the flow. The syringe pump is controlled from the experimental hall and fixed the flow rate to 2 µl/min. The outlet tube is connected to the glass vial. Figures 1b and 1c are the microfluidic devices with a single inlet and double inlets respectively.

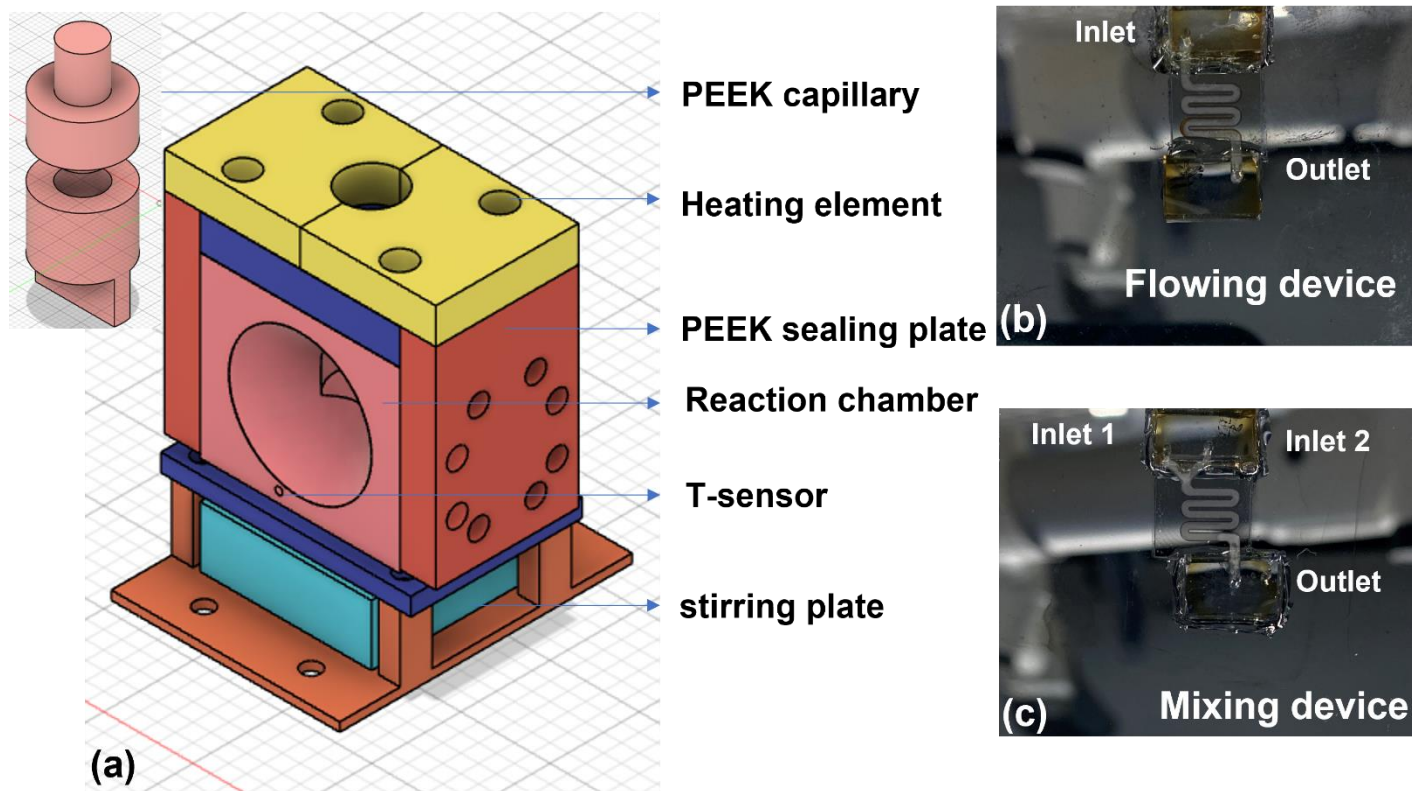


Figure 1 (a) in-situ reaction cell used for the HERFD-XANES measurement for the ZnS and Fe₃S₄ reaction (b) microfluidic flow device with the single inlet and (c) microfluidic flow device with two inlets to mix the two different solutions.

In the second part of the beamtime, we measured the in-situ HERFD-XANES measurement at the Fe K-edge during the synthesis of colloidal Fe₃S₄. The same procedure is followed to prepare the precursor solution as explained above for the ZnS. The precursor solution contains Fe (III) acac₃, thioacetamide and benzyl alcohol. The HERFD-XANES data is acquired during the in-situ reaction from RT to 140 °C with the ramp rate of 10 °C/min and stayed at 140 °C for 90 min. After 40 minutes at 140 °C, the Fe complex is completely converted to Fe₃S₄ and no further changes are found in the spectra. Figure 2 shows the Fe K-edge in-situ HERFD-XANES of Fe₃S₄ data. The detailed data analysis is in progress and we will publish the results soon.

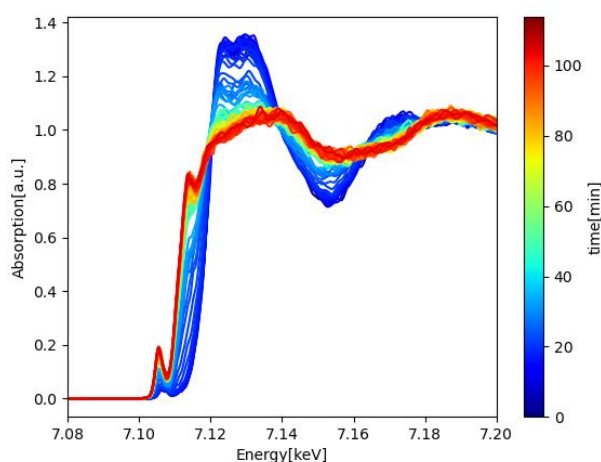


Figure 2. Fe K-edge in-situ HERFD-XANES of Fe₃S₄ colloidal nanoparticles.