ESRF	**Experiment title:** Tracking the structural response of size-selected nanoparticles to electrochemical oxidation using in operando time-resolved grazing incidence high-energy X-ray diffraction	**Experiment number**: CH5521
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Shifts: 15	**Local contact(s)**: Jakub Drnec	*Received at ESRF:*

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Report:

The goal of this beamtime was to determine the structural and morphological response of size-selected metal nanoparticles to oxidizing electrochemical conditions by using operando high-energy X-ray diffraction. We successfully prepared size-selected nanoparticles but the degree of epitaxy did not allow us to perform the study as planned.
In contrast we performed operando HE-XRD experiments on Cu_2O nanocubes (NC) during electrochemical CO_2 reduction reaction (CO_2RR). We studied bare Cu_2O nanocubes and Pd-decorated Cu_2O nanocubes under potentiostatic and potentiodynamic reaction conditions. Therein, we could follow the electrochemical reduction of the Cu_2O under the reducing conditions by recording diffraction pattern during constant CO_2RR potential and for selected increasingly cathodic electrode potentials. In this set of experiments we identified a complete reduction of the Cu_2O in the case of the Pd decoration while a remnant Cu_2O phase was present during CO_2RR without the Pd decoration. We also revealed differences in the structural evolution of the Pd-decorated Cu2O depending on the electrochemical protocoll. In the case of stepwise decrease of the electrode potential we could detect the appearance of a crystalline Pd phase whereas after direct polaization to CO2RR conditions we did not detect a metallic Pd phase.
In addition to the stationary experiments we also recorded diffraction pattern of the Cu_2O NC under potentiodynamic conditions. We previously unravelled that performing CO_2RR under pulsed conditions increases the selectivity towards the desired C_{2+} products like ethanol and ethylene. Thus, we recorded diffraction pattern with millisecond time resolution during 1s potential pulses between reaction conditions and oxidizing conditions. Our data analysis showed an continuous reduction of the Cu_2O to metallic Cu and that the lattice of the Cu responses on a sub-pm length scale to the potential pulses. In contrast, the remnant Cu_2O phases does not follow the electrode potential variations. These operando HE-XRD experiments were the kick-off for further operando X-ray absorption and diffraction studies at other synchrotron facilities (Bessy II

and Petra III) enabling us to follow the Cu redox and Cu lattice response under potentiodynamic CO_2RR conditions in more detail.
In addition to the operando experiments, we recorded a series of *ex situ* diffraction pattern e.g. on PtSnCo nanocubes for electrochemical ethanol oxidation which were included in submitted manuscripts.