

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

**Experiment title:**Structural transformations affecting the CO₂ electroreduction performance of CuO_x nanoparticles**Experiment****number:**

CH-5527

Beamline: ID31	Date of experiment: from: 28 Nov 2018 to: 02 Dec 2018	Date of report: 12.02.19
Shifts: 12	Local contact(s): Isaac Martens, Jakub Drnec	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):***Xingli Wang, TU Berlin*****Elisabeth Hornberger, TU berlin*****Thomas Merzdorf, TU Berlin*****Malte Klingenhof, TU Berlin****Peter Strasser, TU Berlin****Report:**

In this project, we have applied *in operando* wide angle X-ray scattering (WAXS) to study structural transformations and determine the active phase of Cu oxides-derived (OD-Cu) electrocatalysts during electrochemical reduction CO₂ in aqueous electrolyte^[1]. OD-Cu catalysts have been reported to exhibit high catalytic selectivity towards value-added C₂₊ products for CO₂RR, with tunable areal particle density^[2] and surface roughness. However, the nature of the catalytic active sites, such as uncoordinated sites, residual oxides, subsurface oxygen, are still under debate. In the operating condition, the transient changes of products formation on OD-Cu catalysts is directly caused by catalyst surface reconstruction when oxygen is removed. The resulting reduced copper is prone to re-react with oxygen and get corroded in unavoidable oxygen and moisture surrounding. In this case, *in operando* detection techniques are of vital importance in time-scale. For this reason we synthesized free-standing 2-dimensional (2D) copper oxide nanosheets (CuO_x NS), exposing predominantly {001} facets, and investigate CO₂RR performance in both liquid H-cell configuration and industry-relevant micro flow cell. The highly active CuO_x NS are used as a catalyst precursor while exhibit ordinary stability towards C₂H₄. The evolution of initial catalyst phase that undergoes at different overpotentials is investigated with *in operando* WAXS. For electrochemical testing, a catalyst ink was prepared with unsupported catalyst particles and drop casted onto glassy carbon (GC) electrodes. A grazing incident diffraction (GID) cell was necessary due to strong preferential diffraction caused by the stacking of the CuO nanosheets, which excluded the use of transmission setup with the X-ray beam parallel to the stacking direction. Therefore, the experiments were performed with the GID cell, based on thin film concept. A peek foil was used as X-ray window. X-ray attenuation due to the thick electrolyte film was reduced significantly thanks to the high-energy X-ray radiation. In the experiments, three different constant overpotentials and cyclic voltammetry scanning were applied with same CuO_x NS catalyst loadings of 25 μg cm⁻². The electrochemical measurements showed same behaviour with what was observed in our laboratory. Therefore the potential-dependent WAXS was measured from the beginning of Linear Sweep Voltammetry (LSV) and acquired every 3 min during the reduction reaction protocol and in a following constant potential scan, spanning the range from the relative lower potentials to higher overpotentials. Taking the reduction reaction at -0.84 V_{RHE} as a special bias, where showed a considerable C₂H₄ formation but no CH₄, the initial

CuO phase started to vanish during the potential-hold region. The initial CuO phase was reduced within the first 30 min, while a small portion of a residual oxide phase lasted for almost 120 min (Figure 1a). The appearance of a metallic copper phase is particularly evident in the 111 diffraction peak (Figure 1b). The post-formed metallic phase remained unaffected after complete reduction. This transit transformation confirms the necessity to use *in operando* techniques to characterize this metallic phase, which is easily re-oxidised when the potential is stopped. The investigations with different potentials also show the phase evolution speeds up with higher overpotentials, which affects the products distribution.

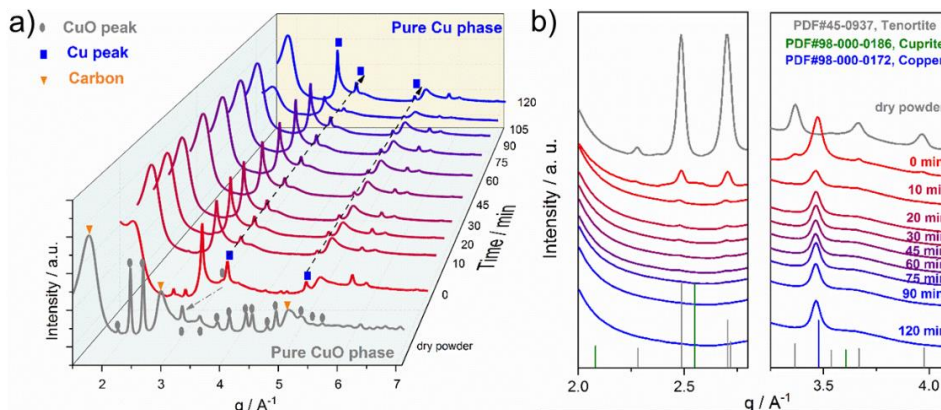


Figure 1: a) In operando WAXS showing the reflections of CuO in CuO_x NS vanishes and metallic copper forms with time at 0.84 V vs. RHE in CO₂-saturated 0.1M KHCO₃. b). Enlarged figures with certain q values.

Besides, the CuO_x NS exhibits strongly preferred orientation when drop casted onto glassy carbon electrodes. The diffraction patterns are mainly contributed by the CuO phase, while a small reflection due to an additional Cu₂O phase is also observed with low angle (Figure 2a). The higher order Cu (I) peaks appear absent. It can be seen that the (002) and (11-1) reflections of Cu (II) exhibit a stronger intensity in the meridional direction, demonstrating that the CuO_x nanosheets are stacked along the <00l> direction and that this one is perpendicular to the incident beam. A partial contour plot is shown in Figure 2b, indicating the coexistence of both the Cu₂O phase and the CuO phase. The distribution of scattering intensity was obtained by integration of the 2D detector GI-WAXS image numerically, which is hardly observed by point-detector in the lab.

In conclusions, *in operando* WAXS revealed to be a powerful technique to trace the phase evolution of CuO_x NS with strongly preferred orientation during operating electrochemical reduction process for CO₂RR, indicating a complete conversion from the initial copper oxide phase to catalytically active metallic copper phase. Together the materials and kinetic catalytic study

presented here on previously unexplored sheet-like CuO_x nanoparticles have established valuable structure-activity-selectivity correlations for future catalyst designs.

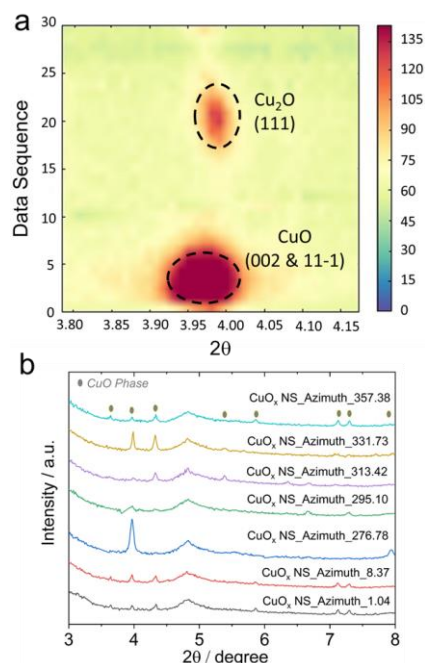


Figure 2: Partial contour plot of CuO_x NS. b) Azimuthally integrated line profiles of as-prepared CuO_x NS.

[1] X. Wang, J. Ferreira de Araújo, W. Ju, A. Bagger, H. Schmies, S. Kuehl, J. Rossmeisl, P. Strasser, *Nat. Nanotechnol.* **2019**, 14, 1063.

[2] X. Wang, A. S. Varela, A. Bergmann, S. Kuehl, P. Strasser, *ChemSusChem.* **2017**, 10, 4642.