EUROPEAN SYNCHROTRON RADIATION FACILITY

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Experiment Report Form

	Experiment title: Local structural and chemical characterization of self-healing copper nanoparticles as catalyst for pharmaceutical and energy applications	**Experiment number**: CH-6251
Beamline:	**Date of experiment**: from: 08/04/2022 to: 11/04/2022	**Date of report**:
Shifts:	**Local contact(s)**: Francesco d'Acapito	*Received at ESRF:*

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Report:

The aim of the experiment was to investigate the oxidation state and coordination geometry of Cu in as synthetized copper nanoparticles (CuNPs) and how they modify during and after the ammonia borane (AB) hydrolysis and hydrogenation reactions. The CuNPs under study have been obtained through the reduction of a mineral, SION-X, by AB. These CuNPs have been shown to be very effective catalysts for AB hydrolysis and hydrogenation reactions of nitroarenes using AB as hydrogen source.

Therefore, the knowledge of the oxidation state of copper and of its first coordination sphere in all these phases is of paramount importance. The experiment was only in part successful.

Three sets of samples were investigated:

1) *SION-X synthesis: $CuSO_4 \cdot 5\ H_2O + NaBH_4$ ---> CuNPs + Na_2SO_4 --> CuNPs + AB --> SION-X.*

2) *AB hydrolysis reaction: SION-X + AB --> SION-X/AB (in H_2O)*
3) *Hydrogenation of nitrobenzene to aniline: $C_6H_5NO_2$ + SION-X/AB --> $C_6H_5NH_2$ (in CH_3OH/H_2O solution in 1: 100 molar ratio)*

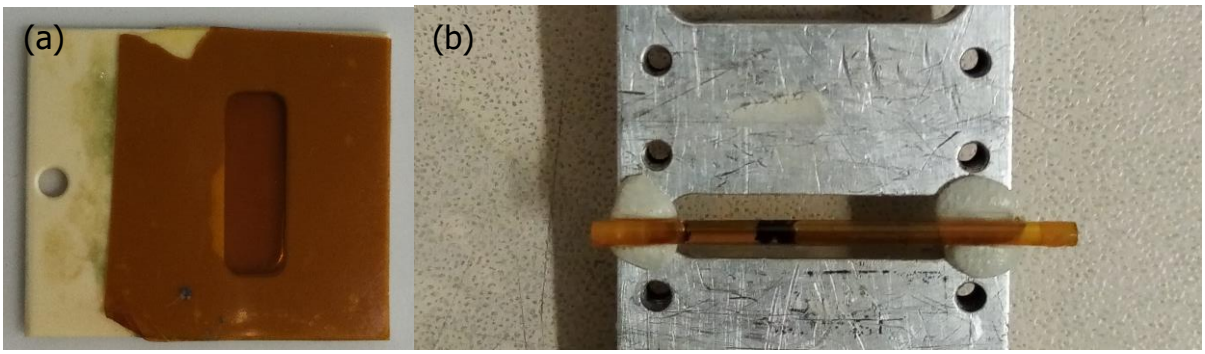

Figure 1. *Picture of the different sample holders used for the collection of the XAS spectra. (a) cell; (b) capillary.*

The samples were all synthetized and measured in their mother or reaction solution. To obtain a sufficiently intense fluorescence signal at the Cu Ka emission line (8.046 keV) the CuNPs suspensions have been prepared to ensure that at least 2 mmol/L of Cu is present. XAS spectra have been acquired in the energy range 8.8 – 10.1 keV at room temperature using a solid-state X-ray fluorescence detector. Five scans have been adopted to increase statistics. To prevent safety hazards due to the toxicity or inflammability of the reactants (e.g., nitrobenzene), chemical preparations and the loading and sealing of the Teflon cells was performed under a chemical hood. However, the quantity of reactants needed was very low (e.g., less than 5 μl of nitroarene in the measurement cells).

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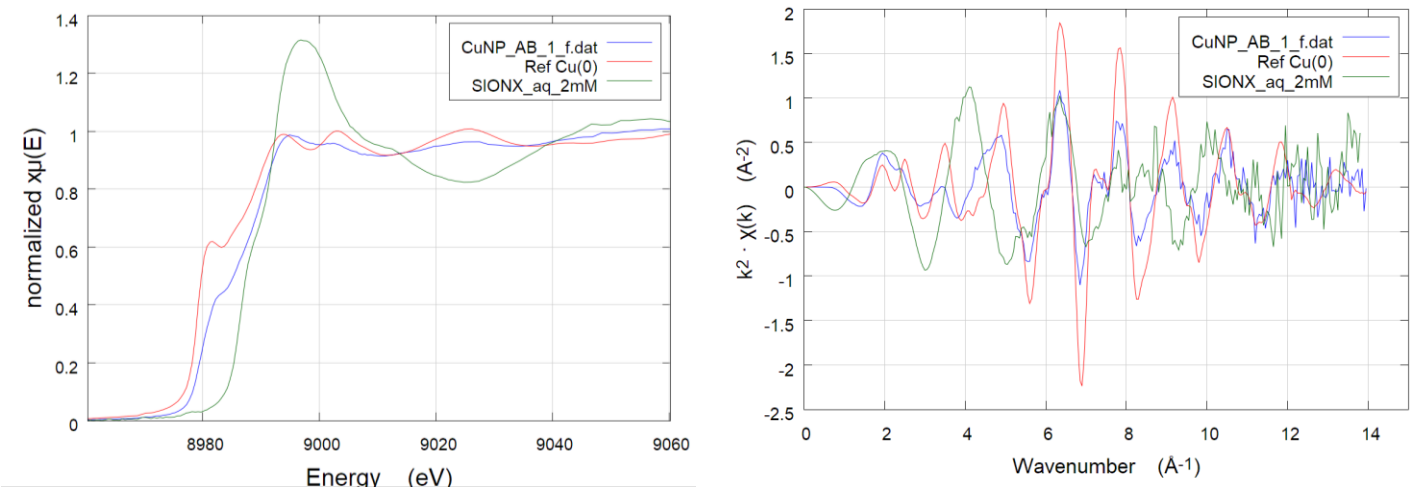
Figure 2. *XAS spectra of Cu K-edge in SION-X and CuNPs from SION-X. Left pane: XANES part of the spectra, indicating that Cu in SION-X is oxidized to 2+, while CuNPs are in the Cu(0) state. Right panel: EXAFS signal indicating that CuNPs have a structure similar to the reference Cu(0) foil, while the structure of SION-X is different (probably more close to the Cu(II) hydroxide). The data analysis is ongoing to confirm the structural parameters and oxidations states.*

, it is reported the set of spectra collected for set 2. These spectra confirm the copper being Cu(II) in SION-X and indicate clearly that in the CuNPs the oxidation state is mainly 0. Previous XPS and Auger measurements performed exposing the CuNPs to the air, suggested the copresence of Cu(0), Cu(I), and Cu(II). The presence of Cu(II) is ruled out by the present measurements that did not required the exposure of the sample to the air. The absence of Cu(II) and the main presence of Cu(0) were also confirmed in the intermediate step of set 1 corresponding to the formation of alternative CuNPs. A full analysis of the samples is ongoing using a dedicated software routine (http://bruceravel.github.io/demeter/documents/Athena/index.html).



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The collection of CuNPs spectra presented several challenges because it was not possible to stir the solution during the spectrum collection and this causes the sedimentation of the NPs, with the consequent change in time of the local concentration of the Cu species and then of the intensity of the spectrum.

In order to solve this problem, we have compared different sample holders (see Figure 1) and verified that the capillaries were more promising for these dispersions. For the capillaries, we have tested different: (i) positioning of the capillary (horizontal or vertical), (ii) % of filled vs. empty volume, (iii) diameters (1.0 vs. 1.5 mm), (iv) different lengths, (v) times after the addition of AB to the solution. This allowed us to determine the optimal conditions (horizontal, 80% filled, 1.0 mm, 6 cm, 30') and to complete the recording of the spectra of set 2. Because this optimization procedure was time consuming we were not able to record the spectra necessary to complete set 3.