

Electronic Supporting Information

For

Controlled formation and density of Cu Nanoparticles on 2D and 3D silica substrate and activity in silicon nanowire growth.

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Experimental procedure.

Nuclear Magnetic Resonance Spectroscopy.

One-dimensional MAS ^1H and ^{13}C CPMAS solid-state NMR spectra were recorded on a Bruker Avance 500 MHz using conventional double resonance 4 mm CP-MAS probe. For these experiments, the MAS frequency was set to 10 kHz and the CP contact time was 2ms.

Transmission electronic microscopy (TEM).

Conventional bright-field TEM micrographs were acquired using a Philips 120 CX electron microscope. The acceleration voltage was 120 kV. The samples were prepared by deposition of the material on a Ni grid covered by a carbon film.

Scanning electronic microscopy (SEM).

SEM micrographs were acquired using a Hitachi 5500a scanning electron microscope. The acceleration voltage was 30 kV with an operating current of 20 μA . The wafers were cut in 0.4x0.4 cm pieces and directly observed.

High angle annular dark-field scanning TEM.

HAADF-STEM micrographs were acquired using a JEOL 2010FEF (FEG -(S)TEM operating at 200 kV) in dark field mode. The samples were prepared by deposition of the material on a Ni grid covered by a carbon film.

X-Ray Photoelectron Spectroscopy.

XPS measurements were carried out with an S-Probe spectrometer from Surface Science Instruments equipped with a monochromated, micro-focussed AlK_{α} source ($h\nu = 1486.6$ eV). Photoelectrons were detected at a take-off angle of 35° with respect to the sample surface by a hemispherical analyser, with an angular acceptance of 35° and pass energy of 25 eV. The overall energy resolution, resulting from monochromator bandpass and electron analyser is of 700 meV. Binding energies are given relative to the Fermi level, subtracting the spectrometer work function, measured with a clean gold surface ($4f_{7/2}$ peak at 83,96 eV). Measurements were performed under controlled Argon atmosphere by preparing and transferring samples with a dedicated suitcase and glove box.

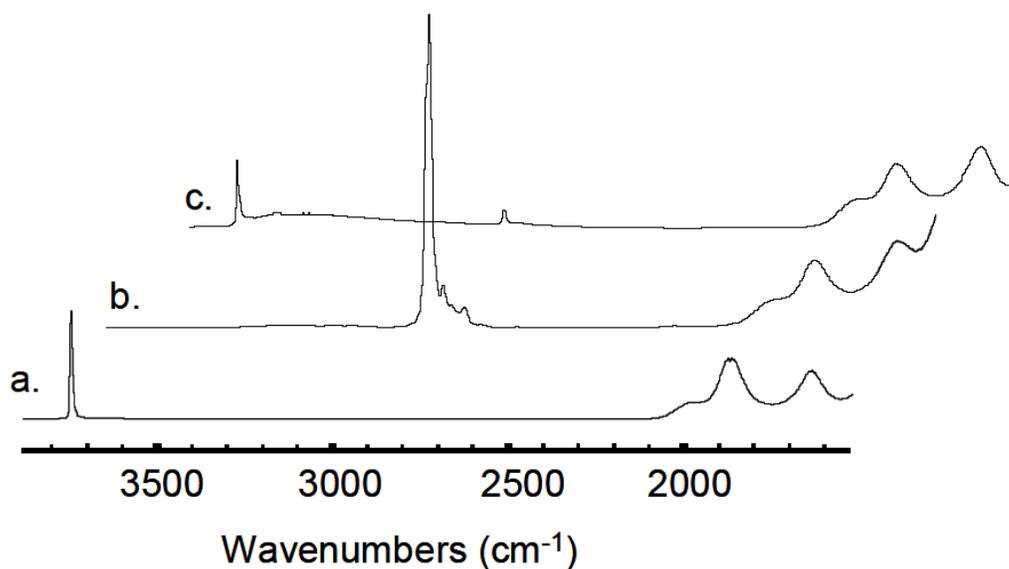
Calculations of Cu nanoparticles density on 3D substrates.

On 3D substrates, the amount of Cu is measured by elemental analysis (%wt_{Cu}, performed at Mikroanalytisches Labor (Remagen-Bandorf, Germany). The 3D substrate surface areas are measured by standard BET treatment of nitrogen adsorption measurement at 77K (S_{BET}). The distribution in nanoparticles size, measured by TEM on each sample, is taken into account to give a mean amount of Cu atoms in a Cu₂O nanoparticles ($Q_{(\text{Cu}/\text{NP})}$).

The final density (D) is given by the relation:

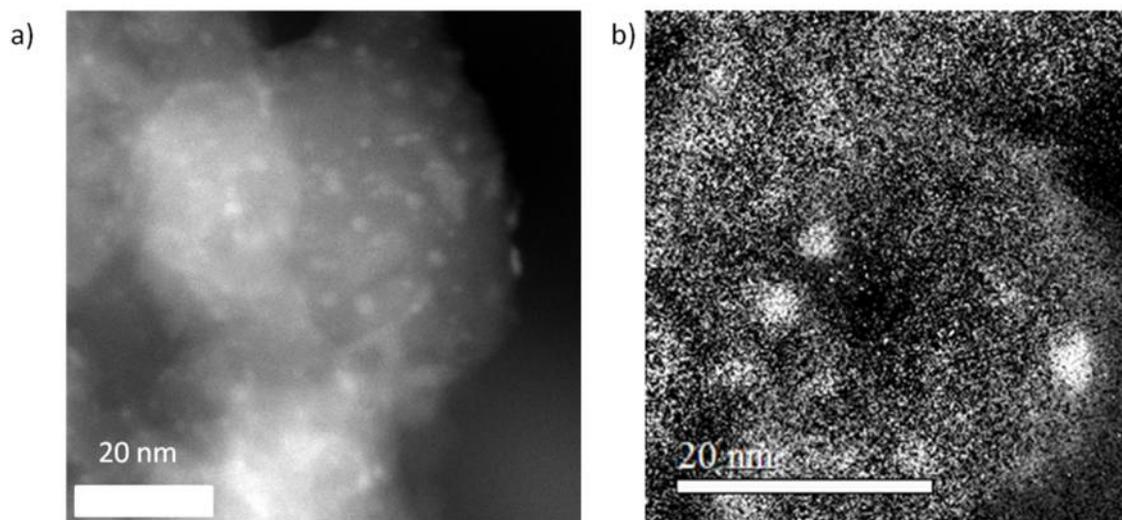
$$D = \% \text{wt}_{\text{Cu}} * N_{\text{a}} / (\text{MM}_{\text{Cu}} * S_{\text{BET}} * Q_{(\text{Cu}/\text{NP})})$$

S1. IR spectroscopy.



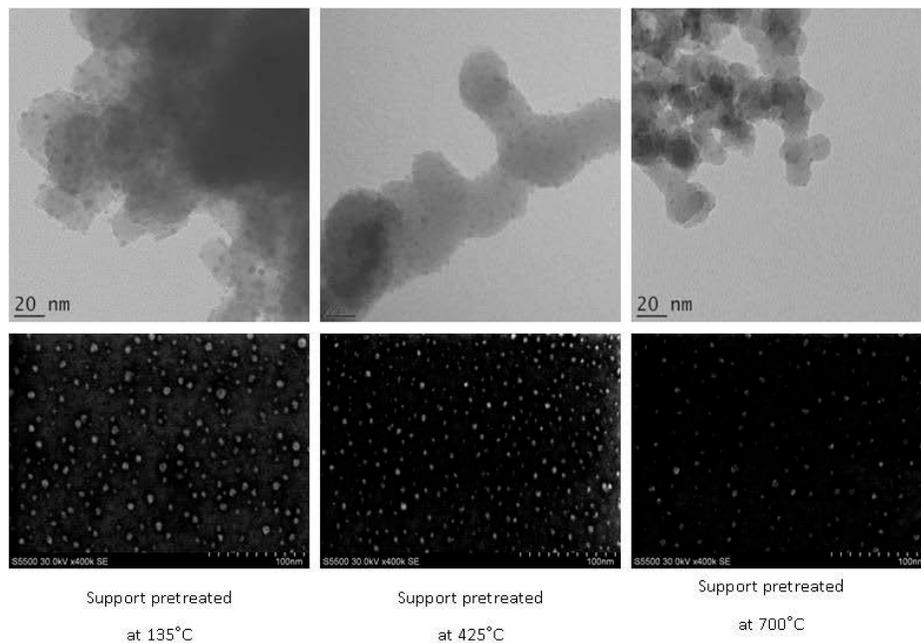
DRIFT spectra of: a. dehydroxylated silica at 973 K, b. [CuOtBu] grafted on silica (**1**), and c. silica supported Cu nanoparticles (spectra shifted for clarity).

S2. a) STEM HAADF and b) Cu EELS mapping at Cu ledge.



a) HAADF-STEM picture and b) Cu EELS mapping at Cu ledge of copper nanoparticles supported on silica nanoparticles dehydroxylated at 973 K

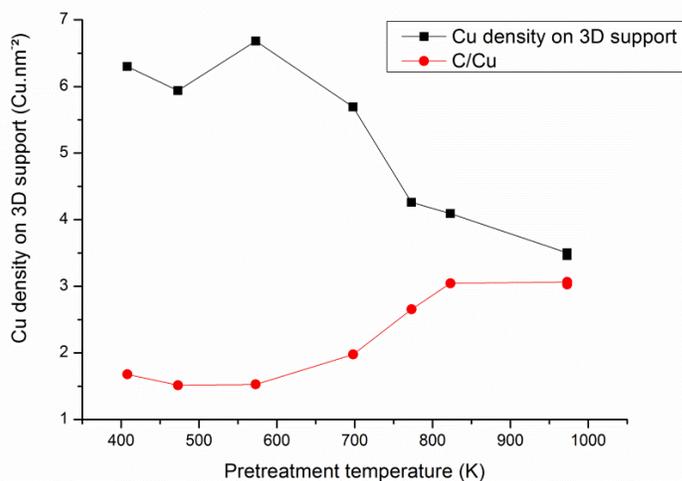
S3. TEM and SEM: Influence of pretreatment temperature



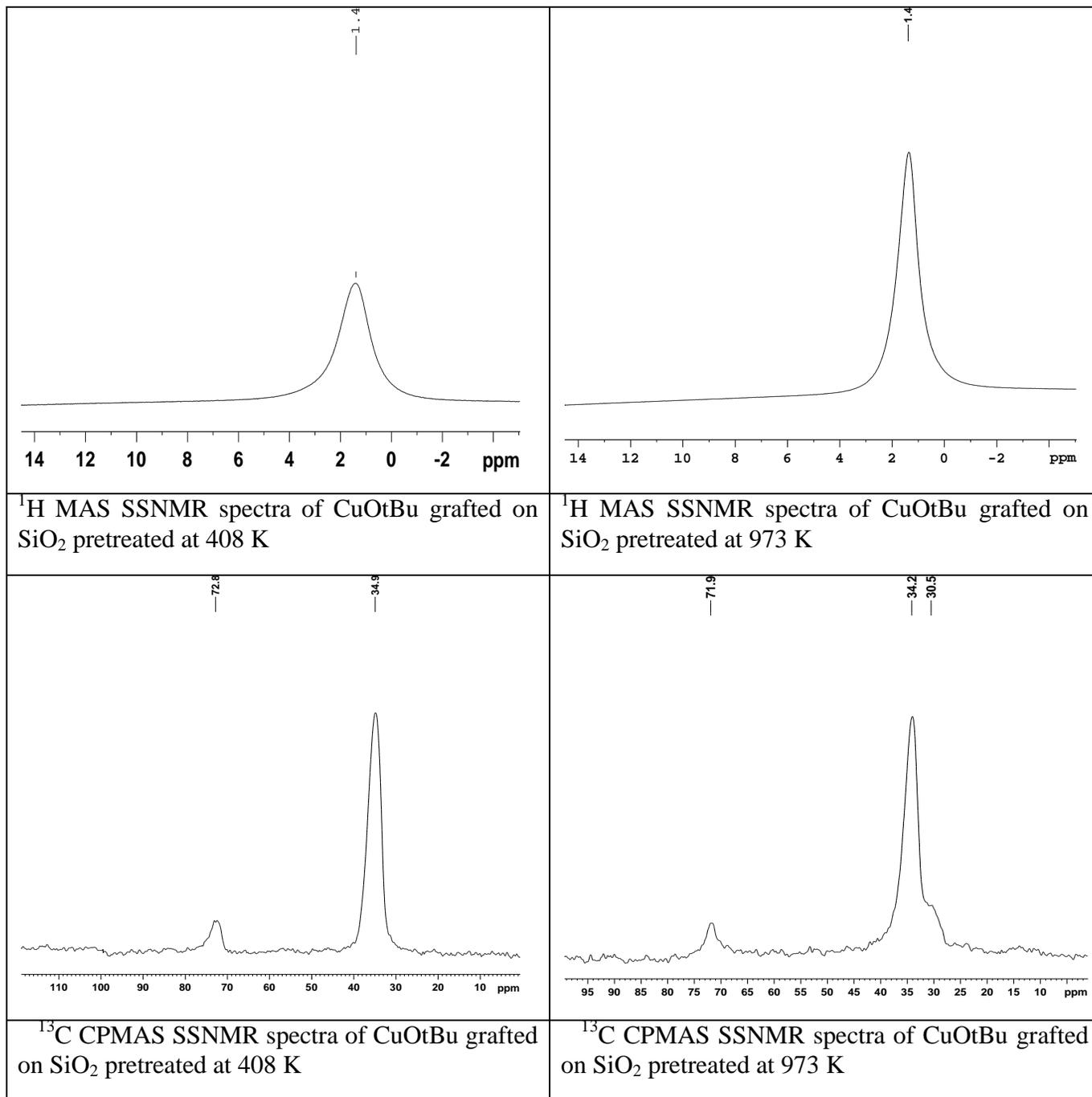
Top : Standard BFTEM pictures of Cu nanoparticles supported on silica (3D).

Bottom : SEM pictures of Cu nanoparticles supported on silica thin film (2D).

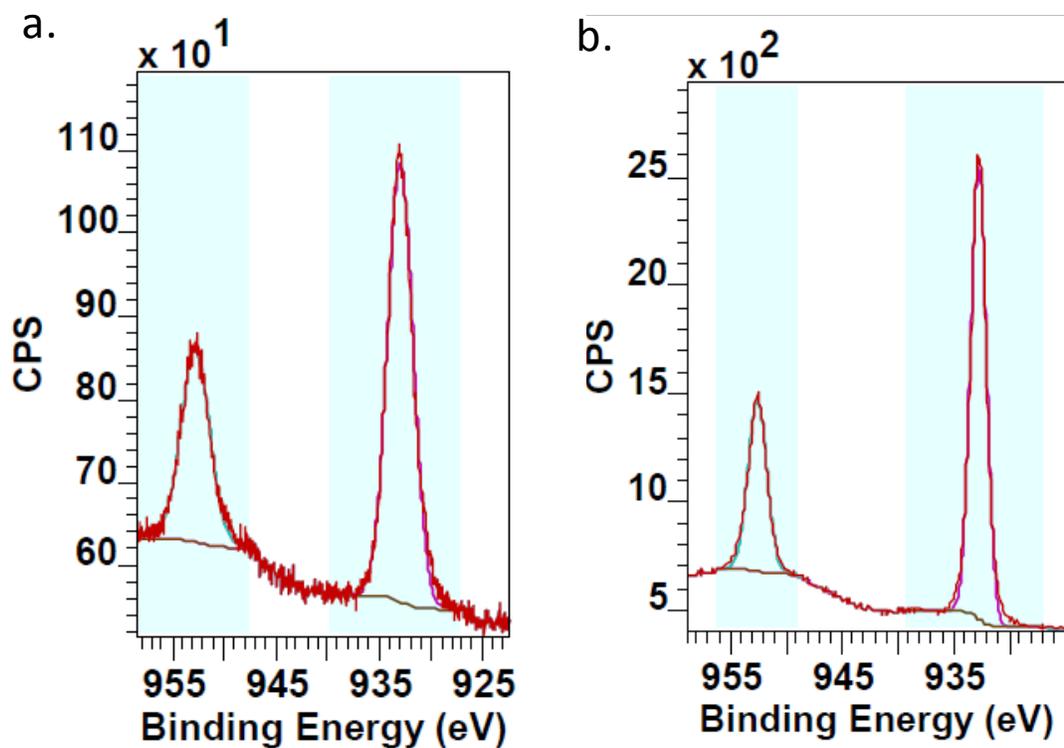
S4. Elemental analysis: Pretreatment temperature effect on Cu density and C/Cu ratio



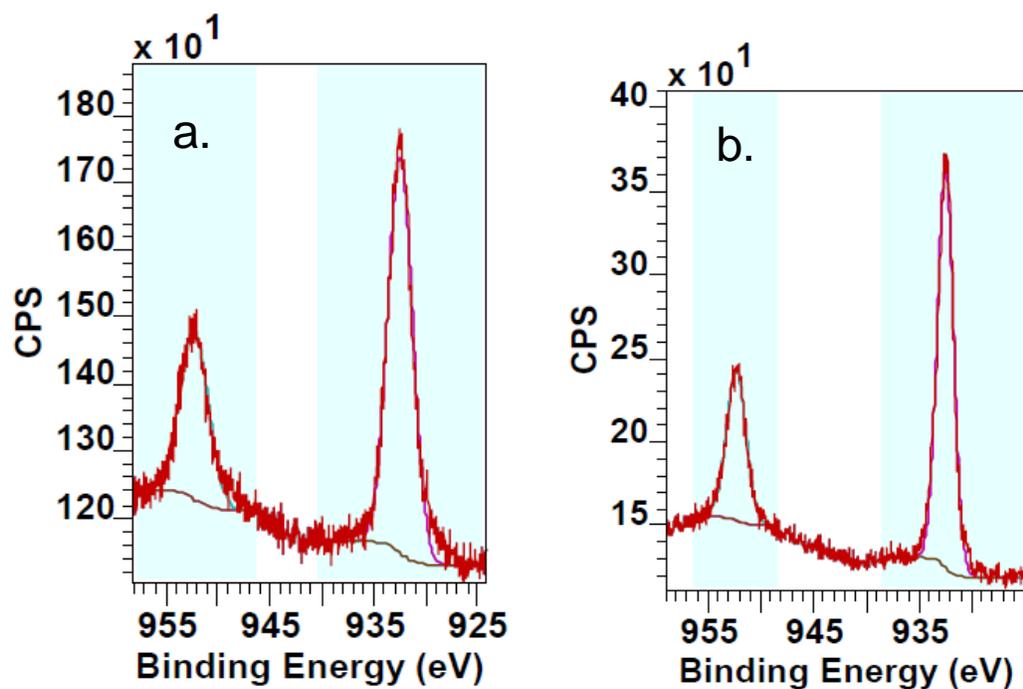
S5. Solid-State NMR spectra.



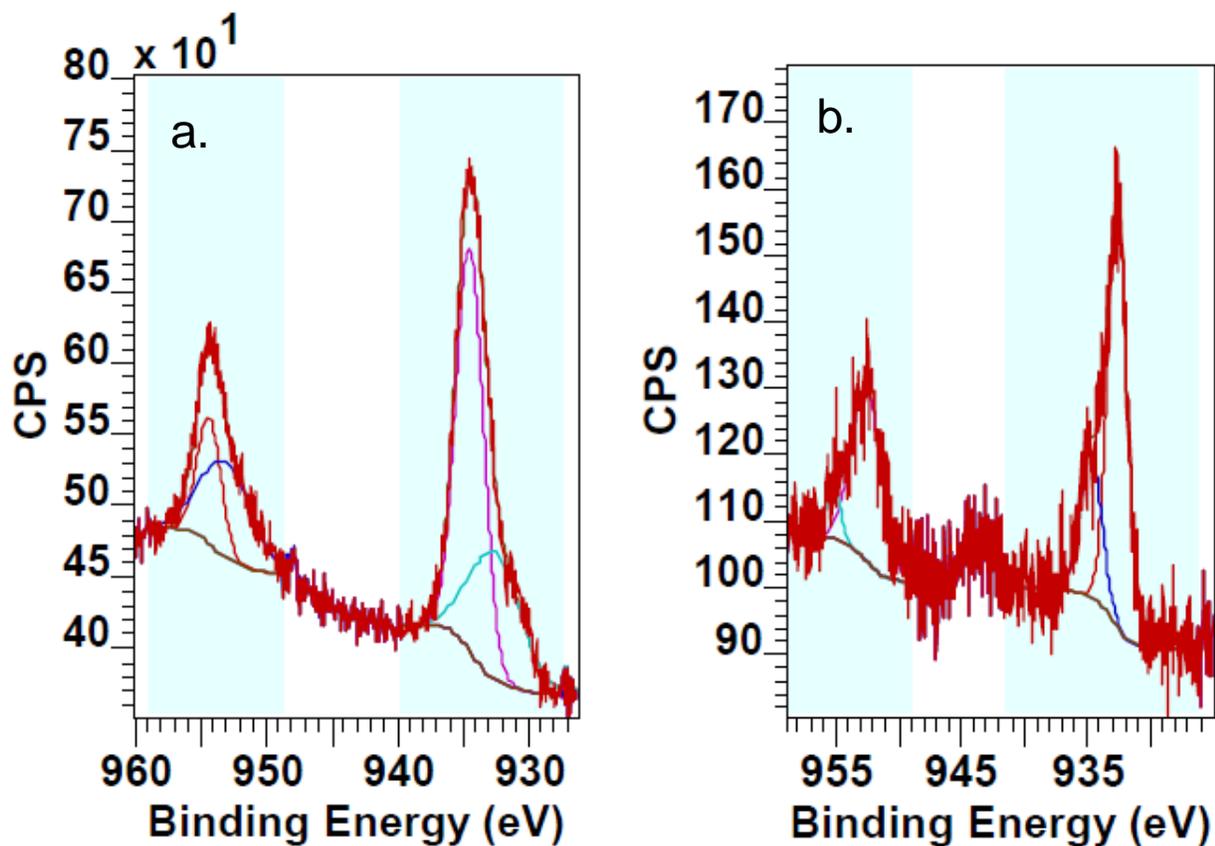
S6. XPS datas.



XPS (Cu 2p) of the Cu(I) grafted species on a. 3D support and b. 2D support

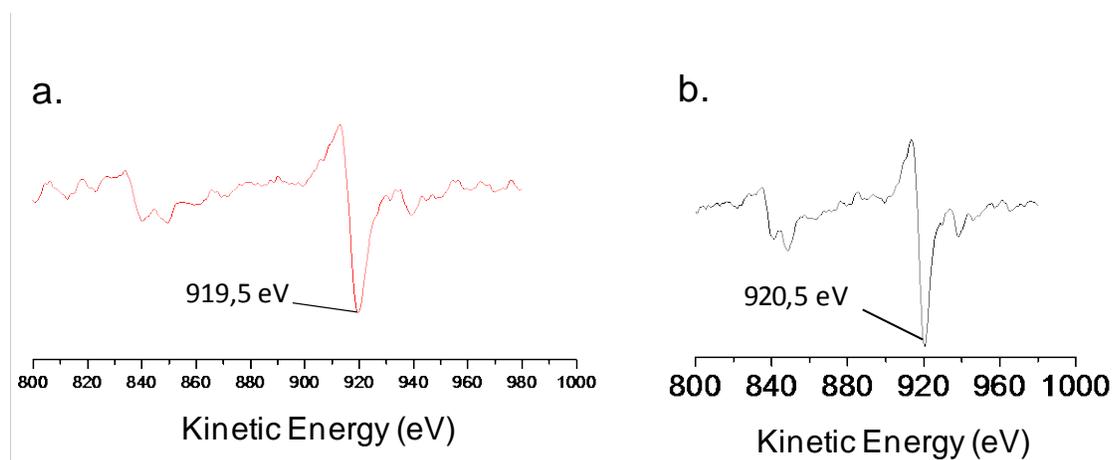


XPS (Cu 2p) of the Cu(0) NPs on a. 3D support and b. 2D support



XPS (Cu 2p) of the oxidized Cu NPs on a. 3D support and b. 2D support.

S7. AES datas.



AES (Cu LMM) of the a. Cu(I) grafted species on a 2D support and b. Cu(0) nanoparticles on a 2D support.