

## Supplementary information

# The role of the copper oxidation state in the electrocatalytic reduction of CO<sub>2</sub> into valuable hydrocarbons

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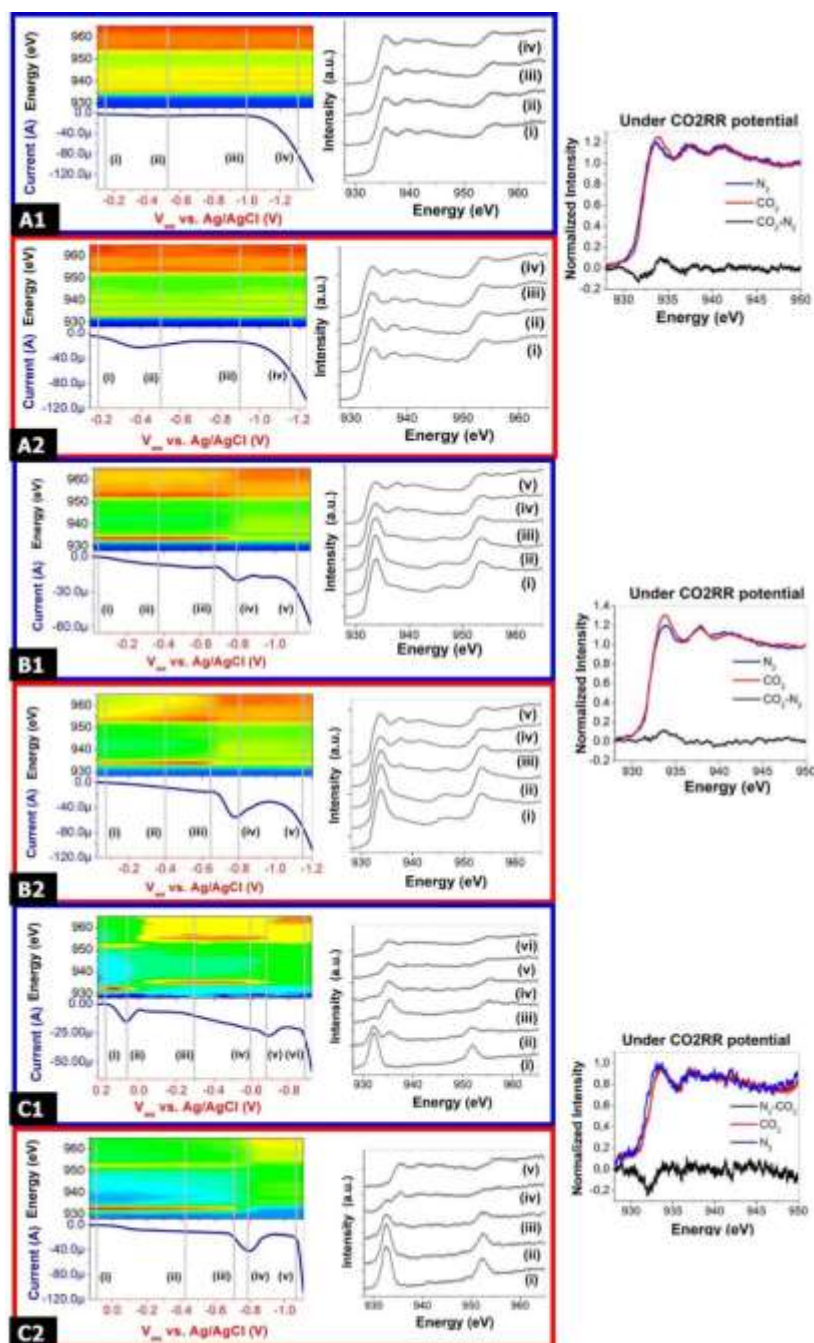
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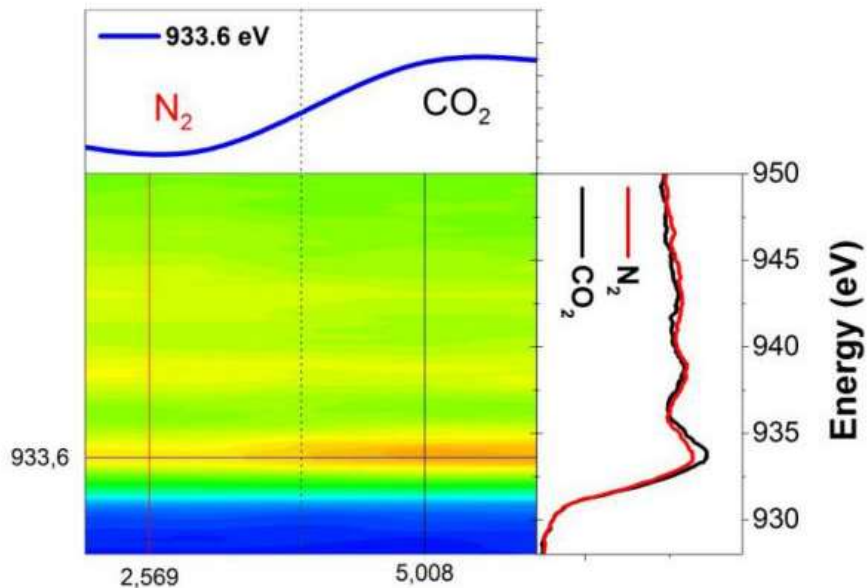
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### ***In situ* flow cell for X-ray spectroscopy**

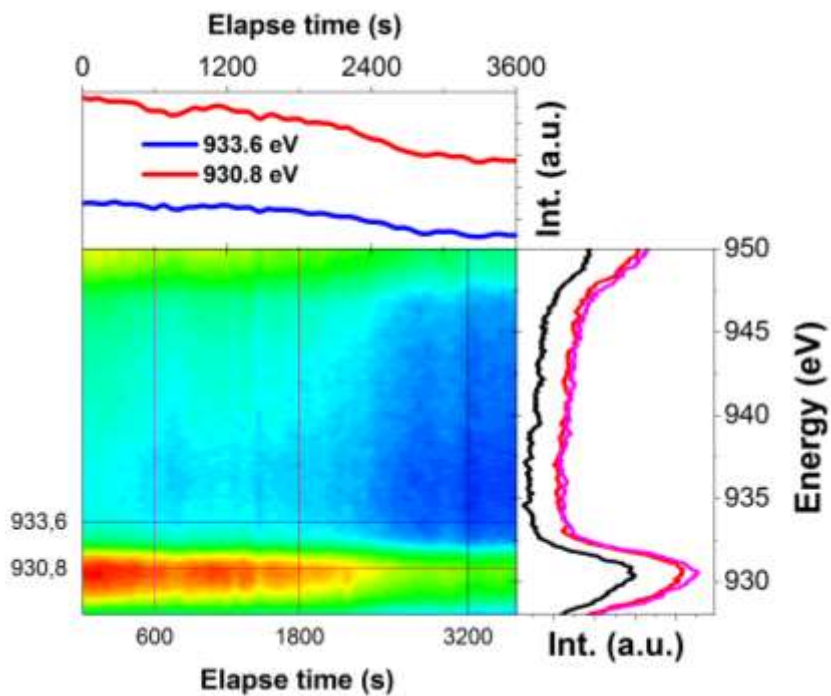
The *in situ* EC flow liquid cell was operated on the main chamber of the beamline 20A1 end station of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu (Taiwan) with a background pressure of  $\sim 10^{-8}$  mbar while the aqueous electrolyte circulated on the back side of a  $\text{SiN}_x$  membrane 100 nm thick (from the company Norcada, Edmonton, Canada). The effective area of the working electrode was  $\sim 2 \text{ mm}^2$ . This membrane is used as working electrode and membrane to separate the liquid from the vacuum side. Hard X-ray absorption measurements at the Cu K-edge were performed at the beamline BL17C1 of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu (Taiwan). The photon source consists of a 25 poles wiggler (W20) with 20 cm period length and a focus spot size of 2 mm x 6 mm. The excitation energy ranges from 4.8 keV up to 14.2 keV. The signal was collected in fluorescence yield mode using an ionization chamber detector. A similar cell to the used in beamline 20A1 was located in the BL17C hutch at 1 bar in air with an effective area of the working electrode of  $\sim 36 \text{ mm}^2$ . The flow of liquid was assured with a peristaltic micro pump, flowing continually around 1 ml/min of electrolyte. In the  $\text{Si}_3\text{N}_4$  membrane a thin Au/Ti thin film was deposited by sputtering using a Cressington 208HR sputter-deposition system. First of all, 3 nm-thick adhesion layer of Ti (99.99%, Elektronen-Optik-Service GmbH, Dortmund, Germany) was deposited in a 0.1 mbar Ar atmosphere at a current of 40 mA during 30 s. After that, a 20 nm-film of Au (99.99%, Elektronen-Optik-Service GmbH, Dortmund, Germany) was deposited in a 0.1 mbar Ar atmosphere at a current of 40 mA during 140 s. It yields the formation of a homogenous polycrystalline thin film used as working electrode 20 nm thick on a  $\text{SiN}_x$  membrane (100 nm), which yields a total signal transmission of  $\sim 74\%$  of the incoming X-ray photons. The X-ray transmission through this membrane is estimated to be approximately equal to 80% of the incoming X-ray. The main body of the cell is made of polyether ether ketone (PEEK) which is electrically insulator and chemically inert.



**Figure S1:** Cu L<sub>2,3</sub>-edges spectra depending on the cathodic polarization in the presence of different electrolytes and initial oxidation state: **A** Cu<sup>0</sup> catalyst **A1** 5 mM KClO<sub>4</sub> saturated with N<sub>2</sub>(gas) and **A2** 5 mM KHCO<sub>3</sub> saturated with CO<sub>2</sub>(gas). **B** Cu<sup>+</sup> catalyst **B1** 5 mM KClO<sub>4</sub> saturated with N<sub>2</sub>(gas) and **B2** 5 mM KHCO<sub>3</sub> saturated with CO<sub>2</sub>(gas). **C** Cu<sup>2+</sup> catalyst **C1** 5 mM KClO<sub>4</sub> saturated with N<sub>2</sub>(gas) and **C2** 5 mM KHCO<sub>3</sub> saturated with CO<sub>2</sub>(gas). Side graphics are the Cu L-edge spectra under the highest cathodic polarization with the different electrolytes in order to compare the formation of surface/sub-surface oxygen species.



**Figure S2:** Cu L<sub>3</sub>-edge of Cu<sup>0</sup> catalyst in presence of N<sub>2</sub> and CO<sub>2</sub> shows the existence of a slightly increase of Cu<sup>+</sup> species in presence of CO<sub>2</sub> ascribed to the existence of dissociative proton-consuming reactive adsorption of CO<sub>2</sub> on copper yielding chemisorbed CO.



**Figure S3:** Cu L<sub>3</sub>-edge depending on elapse time of copper carbonates species in presence of 100 mM HClO<sub>4</sub> acidic media.

### Calculation of the Faradaic efficiency of gas products:

$$f_{gas} = \frac{f_{flow} \times c_{gas} / V_m \times n \times F}{I \times 60} \times 100$$

$f_{gas}$ : Faradaic efficiency of gas product, %;

$f_{flow}$ : flow rate of CO<sub>2</sub>, mL min<sup>-1</sup>;

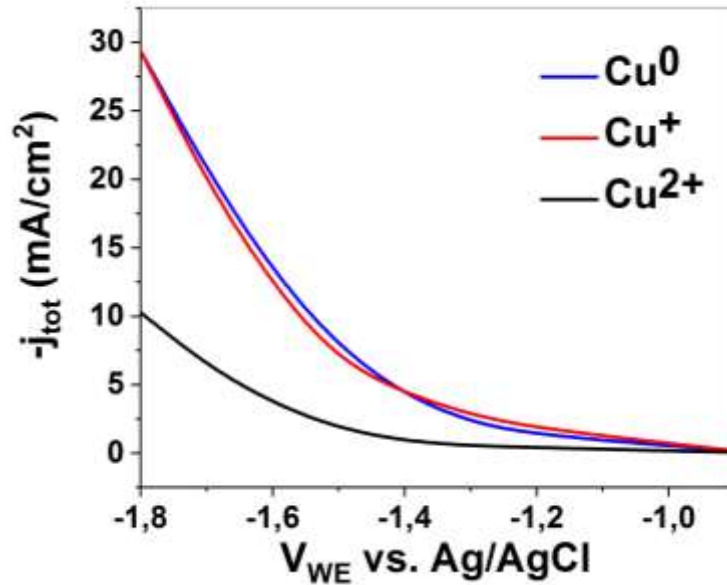
$I$ : electrolysis current at 60 min, A;

$c_{gas}$ : volume ratio of gas product, determined by online GC;

$V_m$ : the molar volume of an ideal gas at 1 atmosphere of pressure, 22400 mL mol<sup>-1</sup>;

$n$ : number of transferred electrons for certain product;

$F$ : Faradaic constant, 96485 C mol<sup>-1</sup>.



**Figure S4:** Density of current for Cu<sup>0</sup>, Cu<sup>+</sup> and Cu<sup>2+</sup> depending on the applied potential in 100 mM KHCO<sub>3</sub> saturated in CO<sub>2</sub>.