

## Supplementary Information (SI)

### *Operando* X-ray absorption spectroscopic flow cell for electrochemical CO<sub>2</sub> reduction: new insight into the role of copper species

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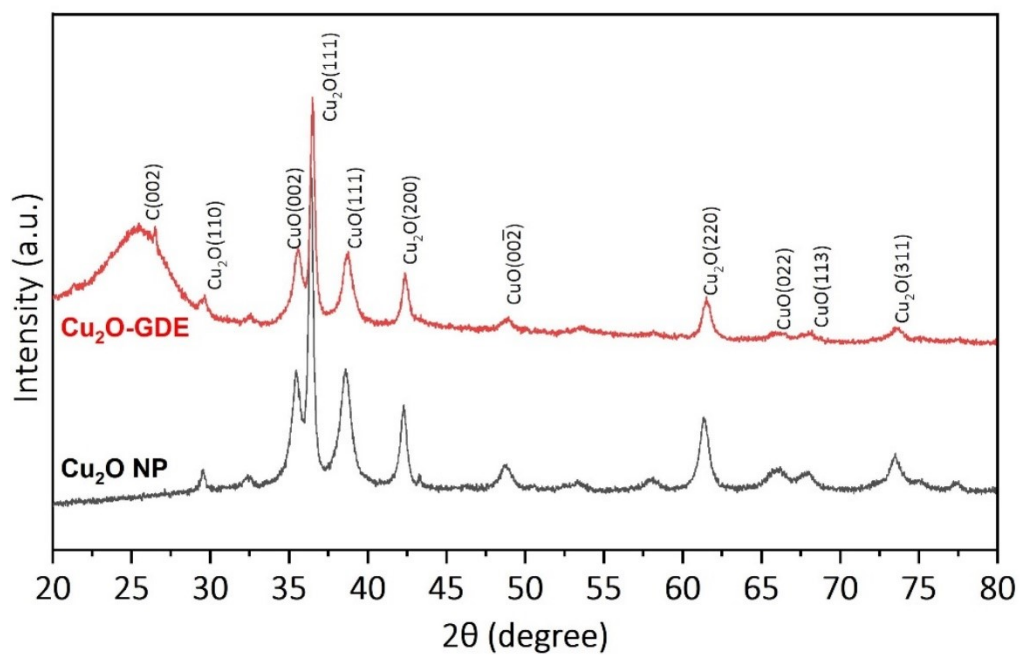


Fig. S1. XRD patterns of the fresh Cu-GDE and commercial  $\text{Cu}_2\text{O}$  nanoparticles.

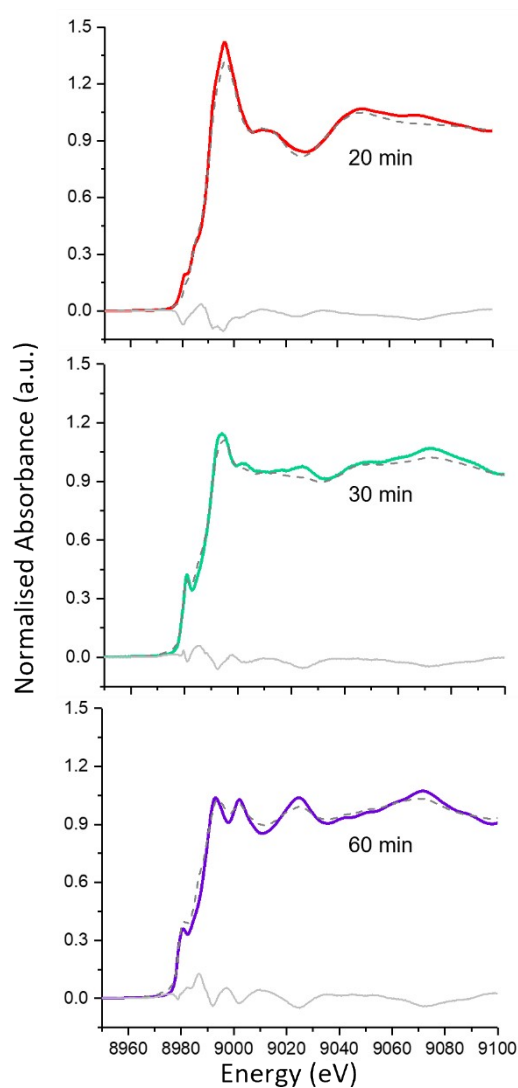


Fig. S2. Linear combination analyses (LCA) of in situ XANES spectra of Cu-GDE during the eCO<sub>2</sub>R reaction. Experimental XANES spectra are shown with solid lines while fits are displayed in dashed lines. Residues of fits are in grey lines at the bottom of the plots, and they indicate that the fit between the experimental data and model compounds employed for LCA is good.

For the XPS fitting, the relative position, area ratio, and FWHM of the peaks were fixed, according to the parameters of Biesinger, assuming the presence of CuO and Cu<sub>2</sub>O (Table S1). For the CuO, the peak shape was a Gaussian-Lorentzian mix, GL(30), while for the Cu(I)/Cu(0) was GL(80).

Table S1. Fitting parameters of the XPS spectra.

	Peak 1			Peak 2			Peak 3			Peak 4			Peak 5		
	position (eV)	FWHM (eV)	area %	position (eV)	FWHM (eV)	area %	position (eV)	FWHM (eV)	area %	position (eV)	FWHM (eV)	area %	position (eV)	FWHM (eV)	area %
Cu(II)	933.1 ±0.1	2.2 ±0.2	31	934.5	3.3	33	940.5	1.1	3	941.7	3.9	28	943.7	1.3	6
Cu(I) /Cu(0)	932.2 ±0.1	1.5 ±0.2	100	-			-			-			-		

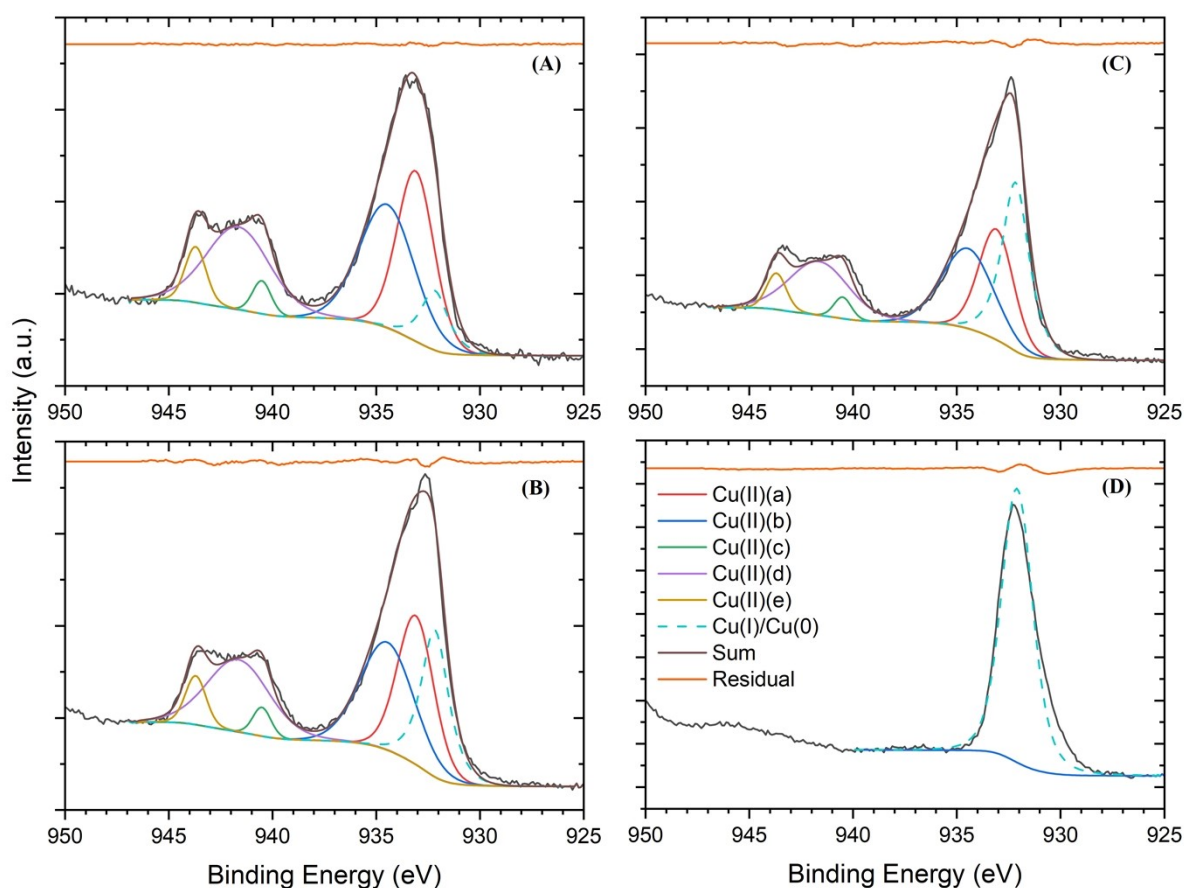


Fig. S3. High resolution quasi *in situ* XPS spectra with individual components of the peak fitting, of Cu 2p of Cu-GDE during the reaction, overall fitting envelope and the residual of the fitting: the Cu-GDE at time 0 (A), 20 (B), 30 (C) and 60 (D) min.

