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Electrocatalytic reduction of carbon dioxide using Cu-based ecocatalysts®

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1. Preparation of ecocatalysts® – Eco1-Cu

1.1. Biomass powder preparation

Eichhornia crassipes and *Mentha aquatica* were cultivated in water tanks in the plant nursery Nymphea (Gard region, France). The aerial parts were removed and the roots were oven-dried at 80 °C during 24 h. The roots were then crushed and sieved through a 1 mm sieve and were used without further purification. Coffee grounds stemming from *Coffea arabica* (Carte Noire coffee) were washed several times with hot water until the filtrate became colorless and were then dried 18 h at 80°C before utilisation.

1.2. Biosorption procedure

1.2.1. Determination of isotherm adsorption models

As a typical procedure, in a 1 L Erlenmeyer flask equipped with a 45 mm triangular magnetic bar, were added 1 L of deionized water (obtained from a Veolia aquadem Purelab flex device, delivering a resistivity of 18 MΩ.cm) and different concentrations of $Cu(NO_3)_2{\cdot}3H_2O$ (19 mg, 57 mg, 285 mg, 760 mg and 1.9 g) (purchased from Sigma-Aldrich company and was used without further purification) in order to obtain solutions containing copper at increasing concentrations of Cu^{2+} (5 ppm, 15 ppm, 75 ppm, 200 ppm and 500 ppm).

The solutions were stirred for 10 min until complete homogenization, then 10 mL of the solution were sampled for MP-AES analysis. 5 g of biomass powder were added and the mixture was stirred at room temperature for 2 h. The mixture was filtered through a cellulose filter by using a Büchner-type filtration device. 10 mL of the filtrate were sampled for MP-AES analysis. The resulting powder was transferred into a crystallizer and was placed into an 80 °C oven for 24 h. The dried powder was heat treated at 550 °C for 4 h. The resulting solid, called Eco1-Cu-XX-XX was transferred into a vial and stored away from moisture.

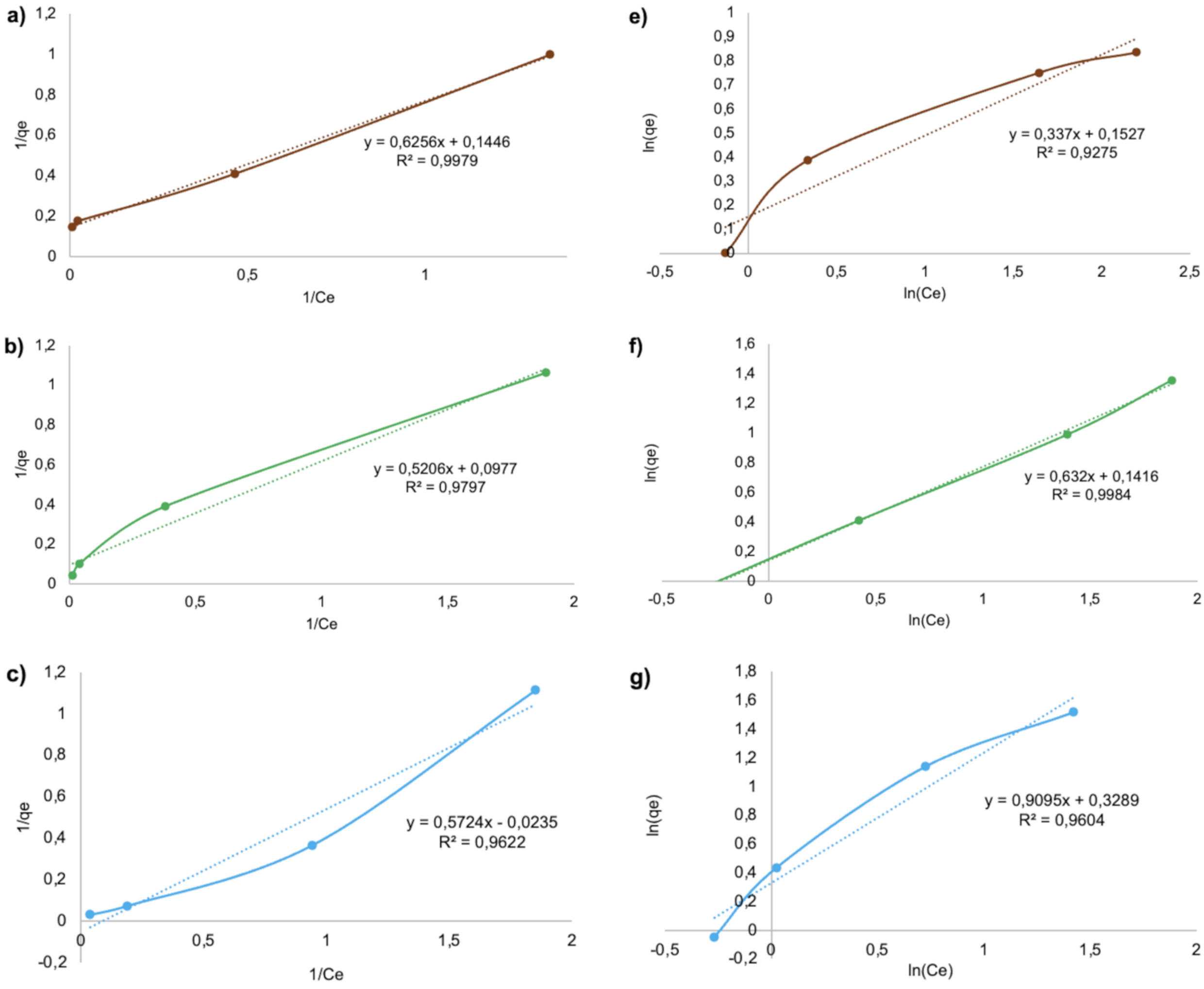

Figure S 1. Theoritical and experimental linearized isotherm for the determination of adsorption model

Table S 1. Biosorption results for the determination of isotherm adsorption models.

Isotherm adsorption model	**Parameters**	**Biomass**		
		M. aquatica	***E. crassipes***	***C. arabica***
Freundlich	r^2	0.9604	**0.9984**	0.9275
	K_f (mg.g-1)	1.388	1.152	1.165
	n	1.100	1.582	2.967
	q_{max} ($mg.g^{-1}$)	164.95	31.69	6.85
Langmuir	r^2	**0.9622**	0.9797	**0.9979**
	K_L (L.mg-1)	0.04	`0.18	0.23
	q_{max} ($mg.g^{-1}$)	42.55	10.23	6.92
experimental	qmax (mg.g-1)	32.95	26.76	6.84

Table S 2. Impact of Cu^{2+} concentration on the composition of Eco1-Cu

Initial concentration of Cu^{2+}($mg.L^{-1}$)	**Element composition (%) of Eco1-Cu**	**Ca**	**Mg**	**Fe**	**Cu**
	CuO NPs	0	0	0	78
5	Eco1-Cu-EI-CR	24	0.45	0.87	0.87
15		24.71	3.29	0.79	2.53
75		22.75	1.83	0.69	8.05
200		16.59	0.58	0.72	19.14
500		16	1	1	**23**
5	Eco1-Cu-ME-AQ	27.9	0.63	0.45	0.24
15		29.54	0.59	0.55	0.78
75		26.93	0.50	0.51	4.9
200		24.52	0.3	0.5	11.2
500		22	0	0	**11**
5	Eco1-Cu-CO-AR	20.51	4.51	0.81	11.58
15		12.72	2.68	0.29	25.71
75		4.26	0.65	0.30	53.61
200		2.97	0.45	0.38	51.65
500		1	0	0	**58**

1.2.2. Biosorption experiments on large scale for the preparation of ecocatalysts®

In a 5 L Erlenmeyer flask equipped with a 45 mm triangular magnetic bar, were added 5 L of deionized water (obtained from a Veolia aquadem Purelab flex device, delivering a resistivity at 18 MΩ.cm) and $Cu(NO_3)_2{\cdot}3H_2O$ (9.5 g, 39.3 mmol), purchased from Sigma-Aldrich company and was used without further purification) in order to obtain a solution containing copper at a concentration of 500 $mg.L^{-1}$. The solution was stirred for 10 min until complete homogenization, then 10 mL of the solution were sampled for MP-AES analysis. 25 g of biomass powder were added and the mixture was stirred at room temperature for 2 h. The mixture was filtered through a cellulose filter by using a Büchner-type filtration device. 10 mL of the filtrate were sampled for MP-AES analysis. The resulting powder was transferred into a crystallizer and was placed into an 80 °C oven for 24 h. The dried powder was heat treated at 550 °C for 4 h. The resulting solid, called Eco1-Cu-XX-XX was transferred into a vial and stored away from moisture.

2. Elemental and structure analysis

2.1. MP-AES analysis of Eco1-Cu

Samples were digested in 10 mL of reversed aqua regia (1:2 hydrochloric acid (37%): nitric acid (65%)) under a microwave-assisted digestion (Multiwave-Go Anton Paar). Samples were filtered and then diluted in 1% aqueous nitric acid. Mineral compositions were determined by using a microwave plasma-atomic emission spectroscopy (MP-AES) 4200 (Agilent Technologies) equipped with a concentric nebulizer and a double-pass cyclonic spray chamber.

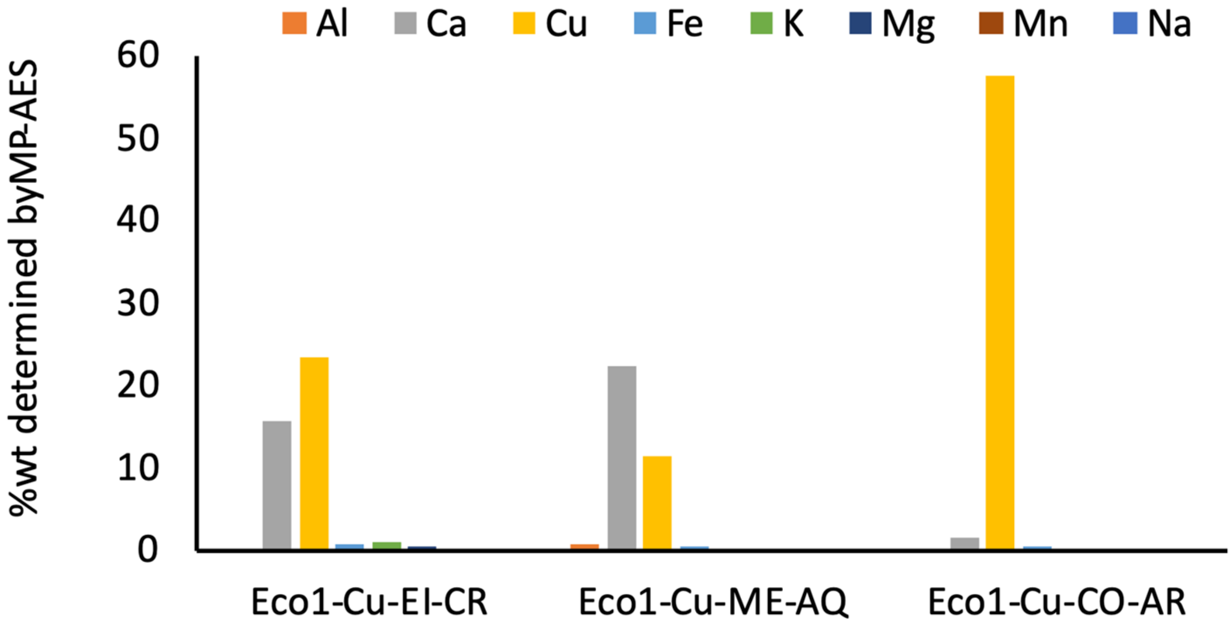

Figure S 2. Elemental composition of Eco1-Cu determined by MP-AES analysis.

2.2. XRF analysis of Eco-Cu1

A PANalytical AXIOS Max spectrometer was used for X-Ray Fluorescence (XRF) analyses, equipped with an SST-mAX^{50} X-ray source specifically adapted for the detection of light element.

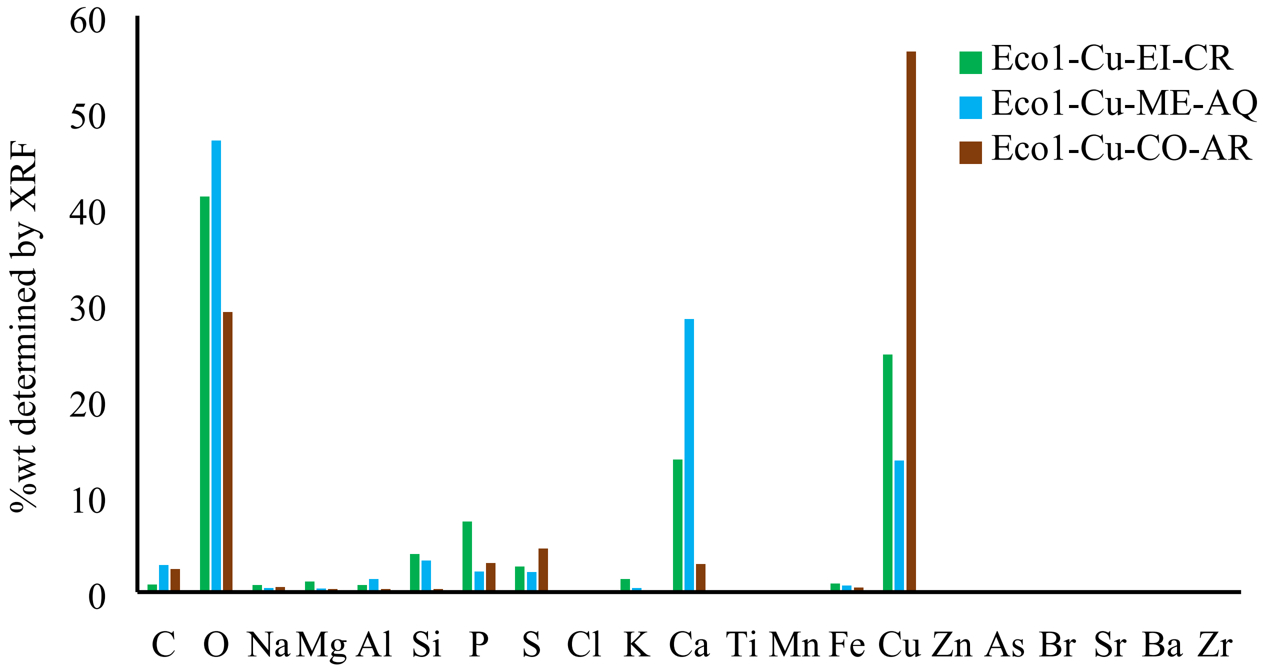

Figure S 3. Elemental composition of Eco1-Cu determined by XRF analysis.

2.3. XRPD analyses of Eco1-Cu

The crystal microstructures of the eco-catalytic powders were analysed by X-Ray Powder Diffraction (XRPD) both with a D6 PHASER, Bruker, (SSD 160-2 LYNXEYE-2 detector), operating at 18 mA and 30 kV from 10 to 70° with a step size of 0.0167, using a Kα1 of copper as source λ = 0.154 nm and a D8 PHASER, Bruker (LYNXEYE XE-T detector) for high copper content samples.

LeBail refinement of the obtained XRPD pattern was performed with a Voigt function using DIFFRACT.EVA.s

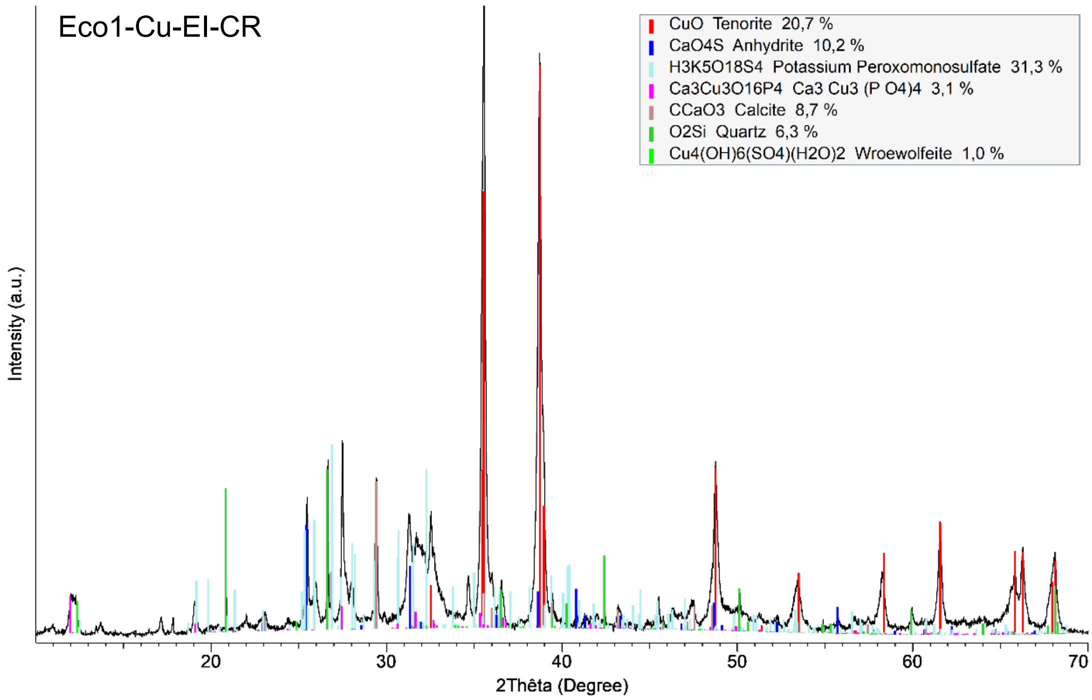

Figure S 4. Diffractogram of Eco1-Cu-EI-CR obtained by XRPD.

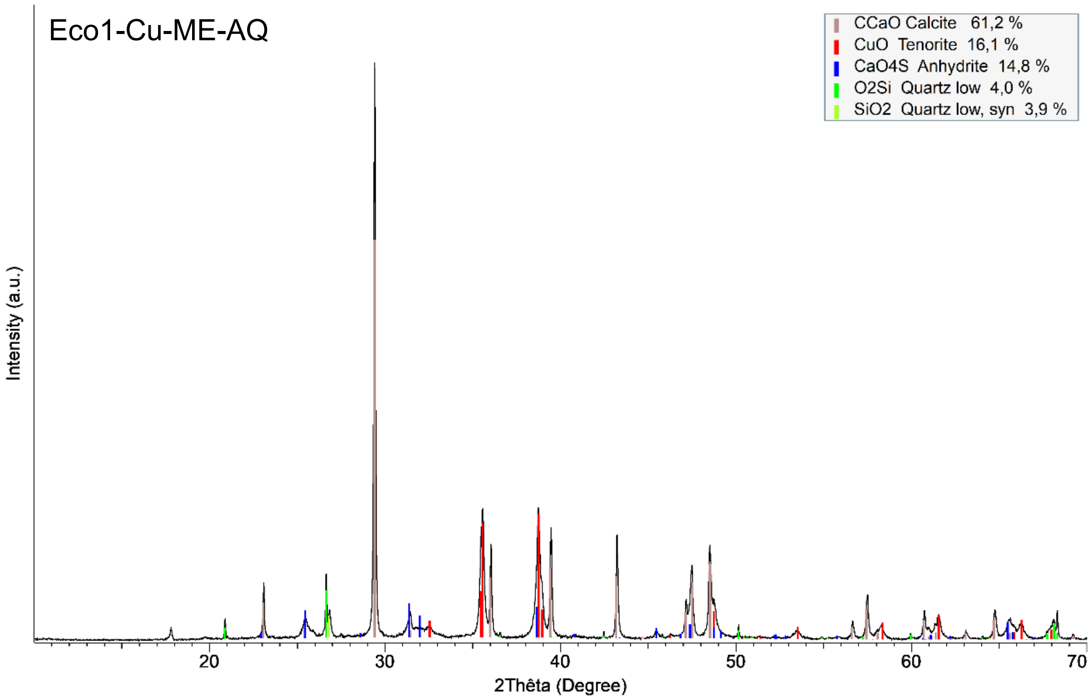

Figure S 5. Diffractogram of Eco1-Cu-ME-AQ obtained by XRPD.

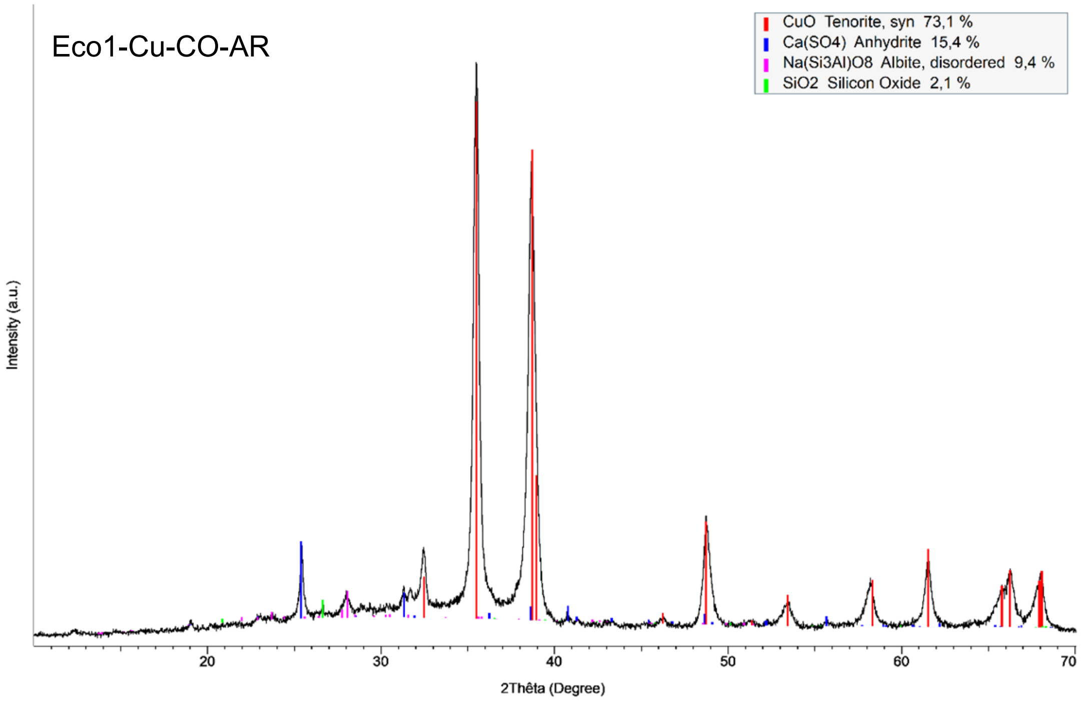

Figure S 6. Diffractogram of Eco1-Cu-CO-AR obtained by XRPD.

2.4. XPS analysis of Eco1-Cu

X-ray Photoelectron Spectroscopy (XPS) measurements were performed on Eco1-Cu and CuO using ESCALAB 250 from Thermo Electron with a monochromatic excitation source, Al Kα x-rays (1486.6 eV) operating at 15 kV and 6 mA. A spot size of 500 µm, a transition energy of 150 eV at a step of 1 eV for the survey and a transition energy of 20 eV at step of 0.1 eV for high-resolution were used. The photoelectron spectra were calibrated using the binding energy of C=C component of C1s at 284.4 eV.

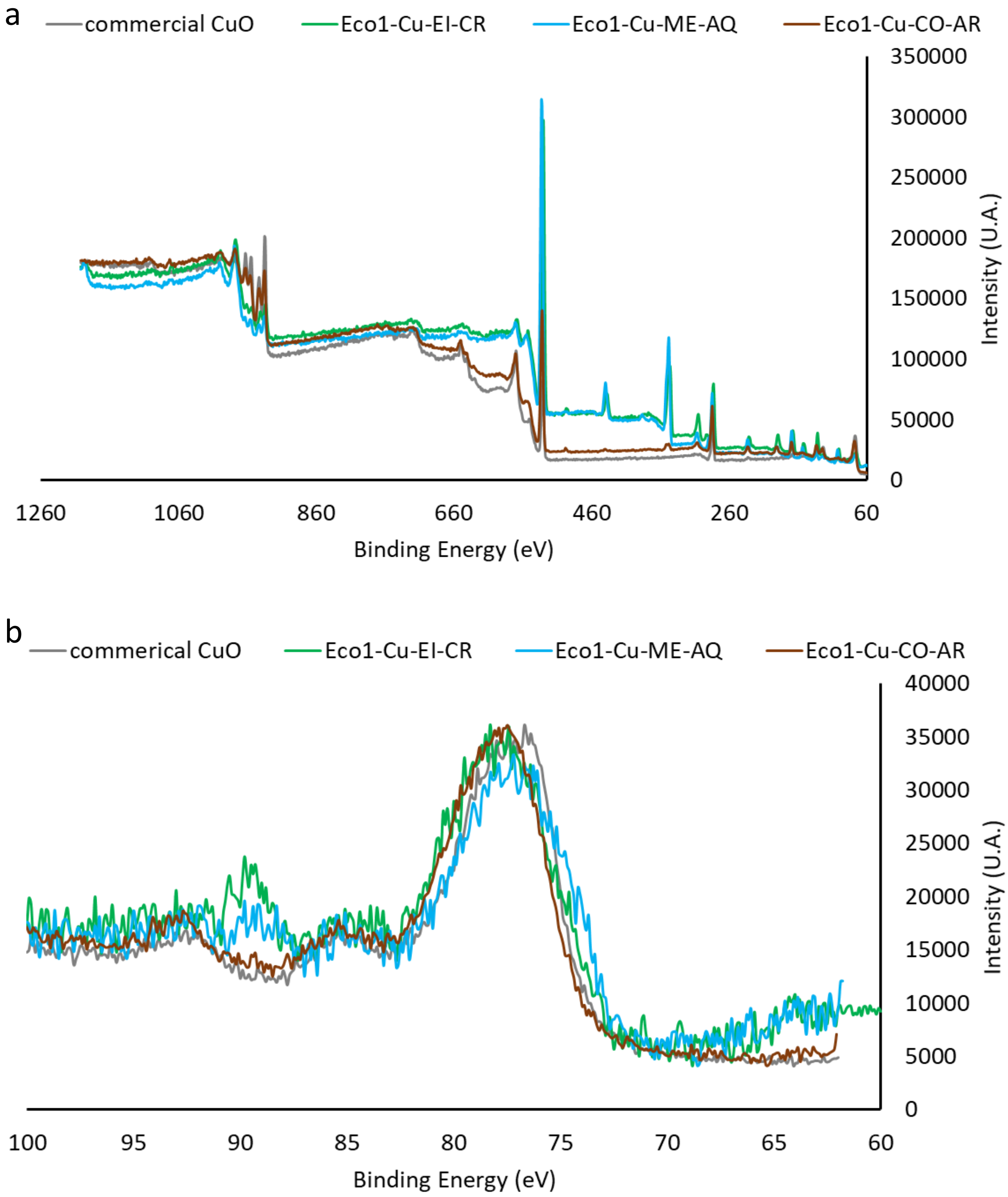

Figure S 7. Superimposition of XPS spectra a. survey and b. Cu-3p for Eco1-Cu samples and commercial pure CuO.

3. Morphological analyses

3.1. SEM-EDX

The powders morphology was characterized with a scanning electron microscope (SEM) (Hitachi S4800, Hitachi High-Tech Corporation, Tokyo, Japan, operating with an acceleration voltage of 2 kV). The chemical composition of ecocatalysts was analyzed using Energy Dispersive X-ray spectroscopy (Detector: Oxford Instruments X-Max^{N} SDD, Abingdon, UK; Microscopy: Zeiss EVO HD15, Jena, Germany). Scanning Electron Microscopy (SEM) associated to Energy Dispersive X-ray (EDX) analysis were performed on catalysts deriving from biomasses of different origins.

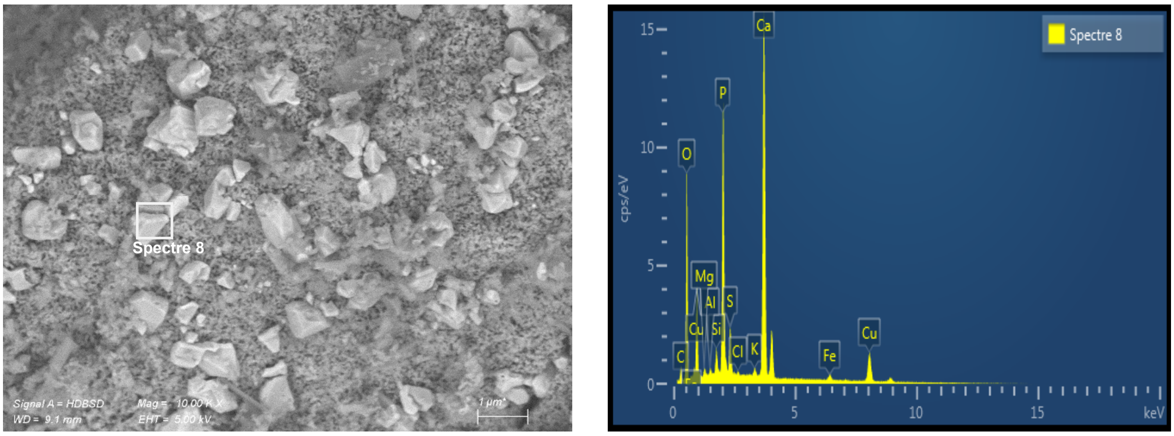

Figure S 8. Representative Scanning Electron Microscopy image and corresponding EDX spectrum of Eco1-Cu-EI-CR.

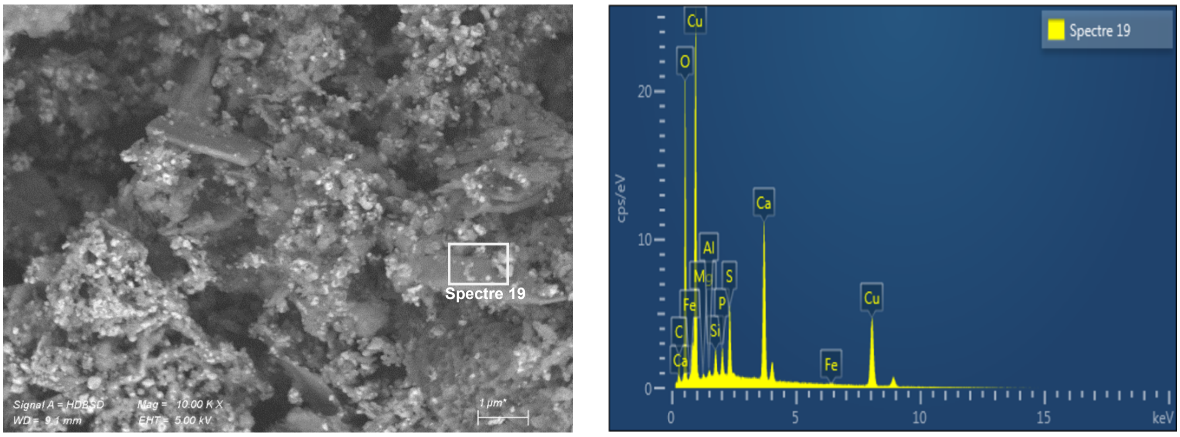

Figure S 9. Representative Scanning Electron Microscopy image and corresponding EDX spectrum of Eco1-Cu-ME-AQ.

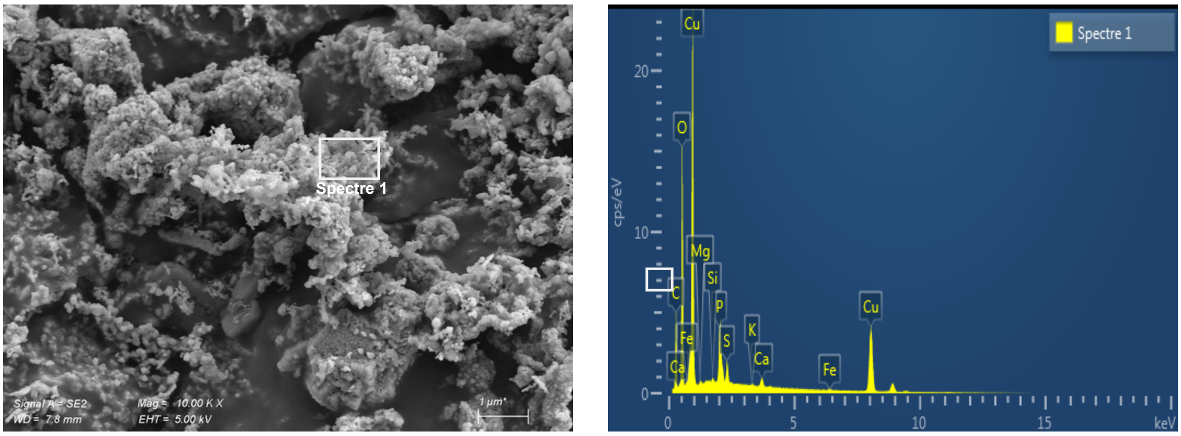

Figure S 10. Representative Scanning Electron Microscopy image and corresponding EDX spectrum of Eco1-Cu-CO-AR.

3.2. BET analysis

BET specific areas are reported in Table S 2. Adsorption and desorption isotherms for Eco1-Cu-EI-CR, Eco1-Cu-ME-AQ and Eco1-Cu-CO-AR were respectively reported on Figures S 9, S 10, S 11).

Table S 3: BET specific areas of the different ecocatalysts

Ecocatalyst	BET specific area $m^2.g^{-1}$
Eco1-Cu-EI-CR	12.5207
Eco1-Cu-ME-AQ	11.4141
Eco1-Cu-CO-AR	0.8632

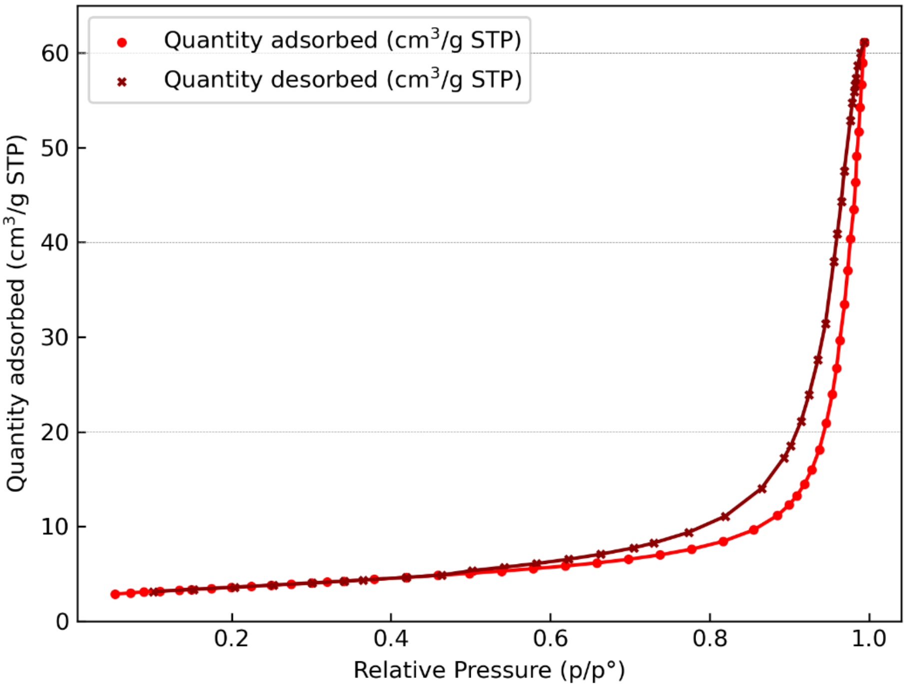

Figure S 11. BET adsorption and desorption curves of Eco1-Cu-EI-CR

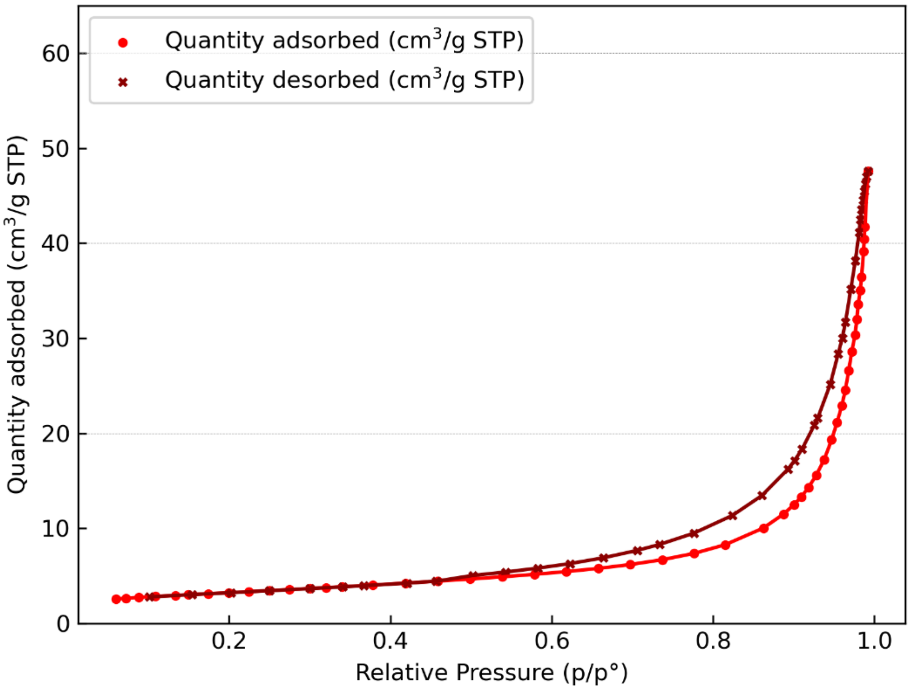

Figure S 12. BET adsorption and desorption curves of Eco1-Cu-ME-AQ

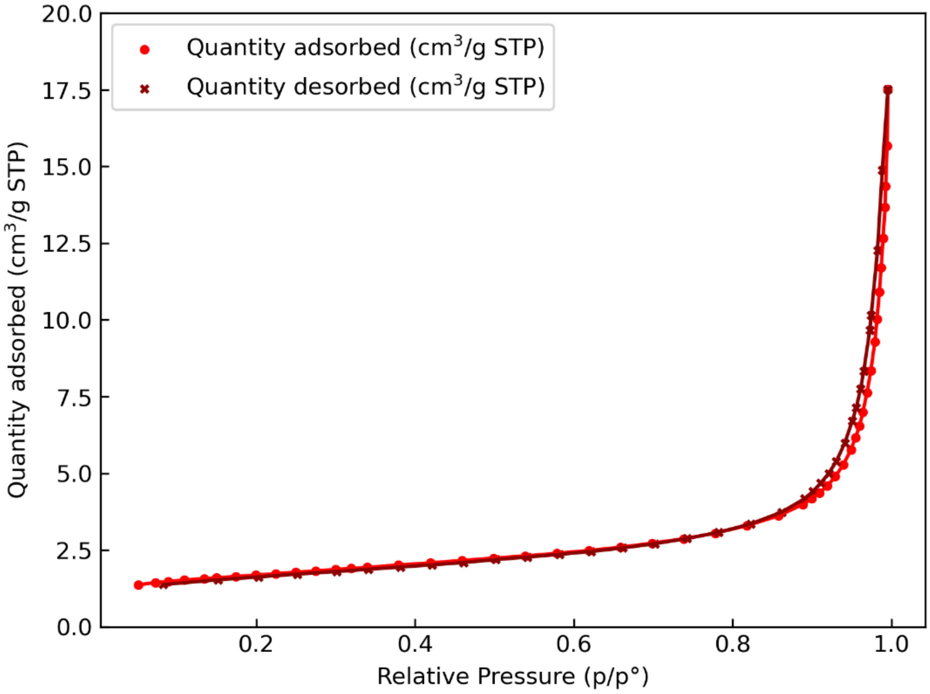

Figure S 13. BET adsorption and desorption curves of Eco1-Cu-CO-AR

4. Electrochemical experiments:

4.1 Preparation of gas-diffusion electrode:

A suspension was prepared as following, 1 mg of catalyst powder (the thus obtained ecocatalysts® – Eco1-Cu, Cu or CuO NPs from Sigma-Aldrich) with 5 µL solution of Nafion 5% (Sigma-Aldrich) and 100 µL of absolute ethanol (Carlo Ebra). Then the suspension was drop-casted onto a 1 cm^2 gas diffusion layer (GDL-AvCarb GDS5130, Dioxide Materials) heated on a hot plate at 60 °C to obtain a load of 0.75-1.2 mg of catalyst / 1 cm^2 of GDL. This modified GDL was then used as the cathode in electrochemical CO_2 reduction.

4.2 Method of electrochemical measurement:

The electrochemical measurements were done through a multichannel potentiostat (Bio-Logic VMP3). To set up the reactor, the cathode, an anion exchange membrane (AEM; Sustainion, X37-50 Grade T, Dioxide Materials) and a Ni foam (Goodfellow, 99.5%) of 1 cm2 were sequentially assembled in a flow cell reactor (Sphere Energy) with some layers of silicon foil placed in between to avoid gas and liquid leakages. A leak-free reference Ag/AgCl (LF-1-45, 1 mm OD, 45 Barrrel, Innovative Instruments) was also inserted to the flow cell. As for the electrolyte, aqueous solutions of KOH 1 M prepared from KOH (powder for synthesis, Sigma-Aldrich) were used as the electrolyte and was circulated with a flow rate of 15 $ml.min^{-1}$. For CO_2 reduction, CO_2 gas (99.998%, Linde) was fed to the back side of the gas diffusion electrode and CO_2 flow rate was regulated at 10 ml.min-1. Controlled-current electrolysis was carried out at current densities varying between -100 and -200 $mA.cm^{-2}$.

4.3 CO_2 reduction products quantification:

Gaseous products: An on-line gas chromatograph (SRI instruments, MG#5 GC, Ar carrier) was employed to quantify the amounts of generated C_2H_4, H_2, CO and CH4. Quantification of H2 was performed by a thermal conductivity detector and a HaySepD precolumn attached to a 3 m molecular sieve column was used to separate H2 from the other gases. Quantification of carbon-based products were carried out by a flame-ionization detector. CO and CH_4 were separated using a 3 m molecular sieve column. C_2H_4 and C_2H_6 were separated using a 5 m HaySepD column. The GC was calibrated by using a gas mixture at different concentrations.

Liquid products: The amounts of liquid products were determined by proton nuclear magnetic resonance spectroscopy (1H-NMR; Bruker Avance III 300 MHz, 300 K). 400 µL of reacted catholyte, 100 µL D_2O (Eurisotop, 99.90%) as a locking solvent, and 100 µL of 5 mM aqueous solution of terephthalic acid prepared from terephthalic acid (Sigma-Aldrich, 98%) as a reference were mixed together for the quantification. The water peak from each spectrum43 was eliminated by a Pre- SAT180 water suppression method.

Faradaic efficiencies of the products were calculated by the equation below.

$$FE_x(\%) = \frac{n_x \times n_{e^-x} \times F}{Q} \times 100$$

nx is the amount of product x (mol), ne⁻x is the number of electrons required to generate product x from CO_2 or H_2O, F is the Faraday constant (96500 C.mol–1), Q is the charge passed to generate n_x.

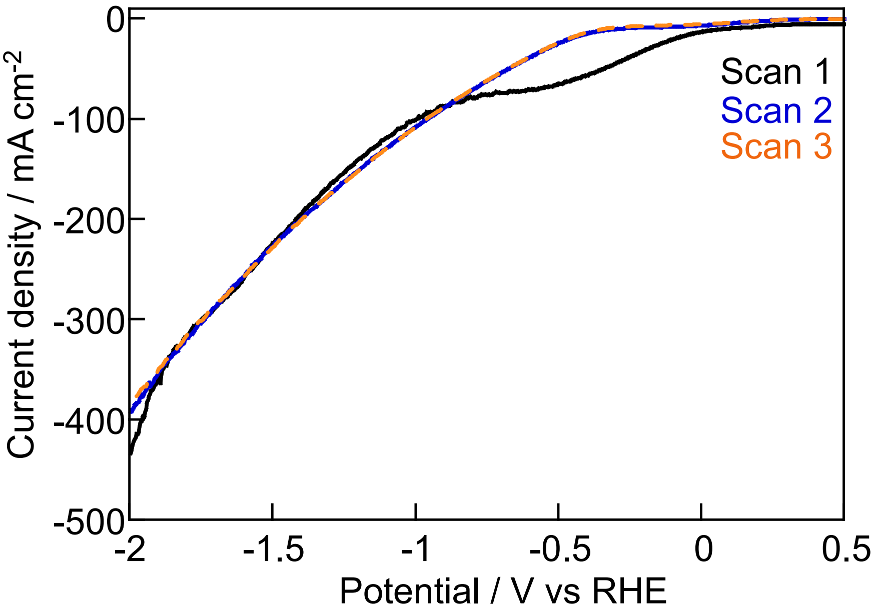

Figure S 14. LSVs of Eco1-Cu-CO-AR catalyst in KOH 1 M, CO2 flow rate: 10 ml min^{-1}.

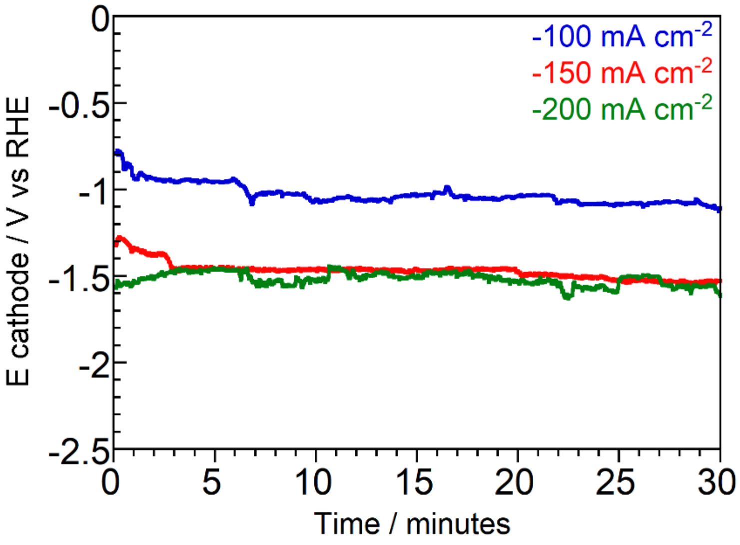

Figure S 15. CO_2 electrolysis using Eco1-Cu-CO-AR in KOH (1 M), CO_2 flow rate: 10 mL.min-1, applied current density: -100 to -200 mA.cm-2, catalyst loading: 1.2 mg.cm^{-2}.

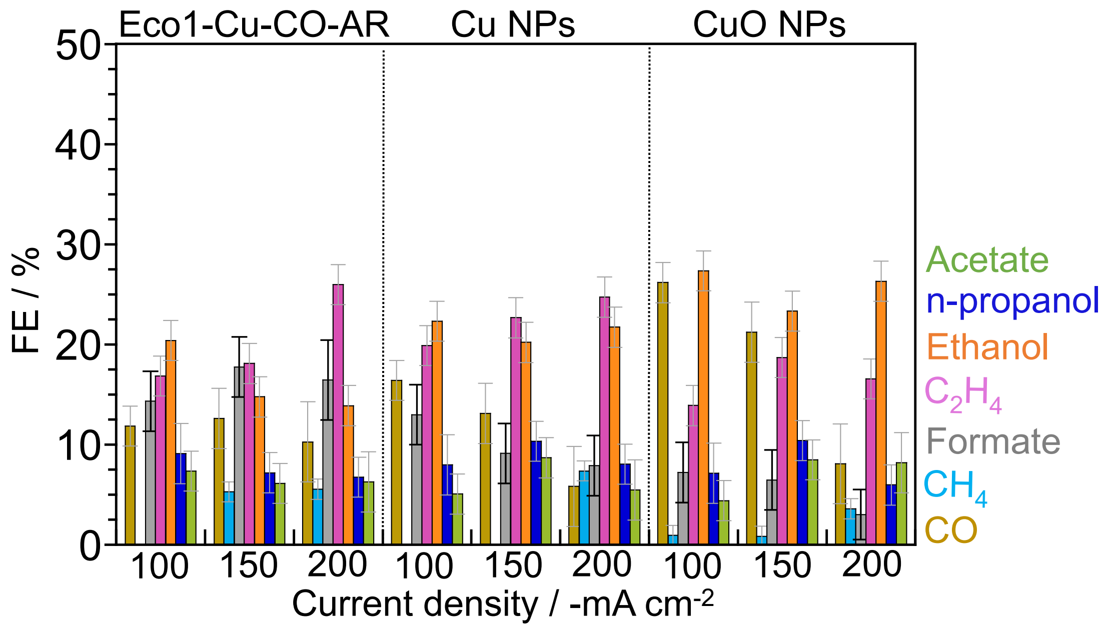

Figure S 16. Faradic Efficiencies for each carbonaceous product derived from CO_2RR using Eco1-Cu-CO-AR, commercial Cu NPs and CuO NPs in KOH (1 M), CO_2 flow rate: 10 mL.min^{-1}, catalyst loading: 1.2 mg.cm^{-2}.

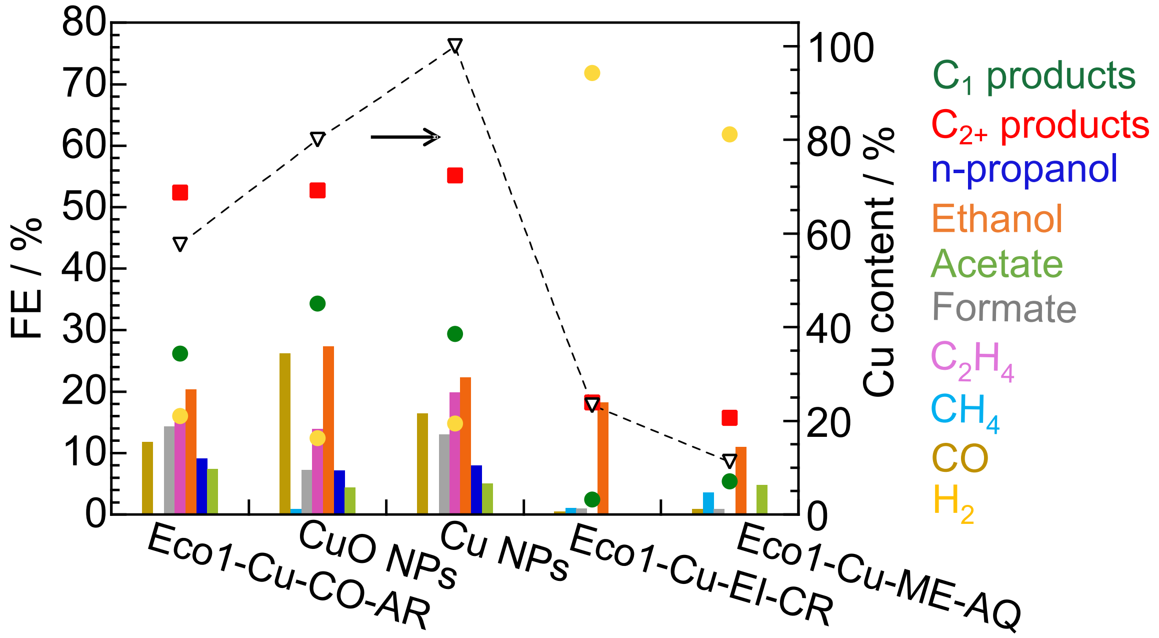

Figure S 17. Faradic efficiencies for CO2R products and Cu content, determined by XRF, of ecocatalysts and commercial Cu and CuO catalysts. Catalyst loading: 1.2 mg cm-2, KOH 1 M, CO2 flow rate: 10 ml min-1, applied current density: -100 mA cm^{-2}

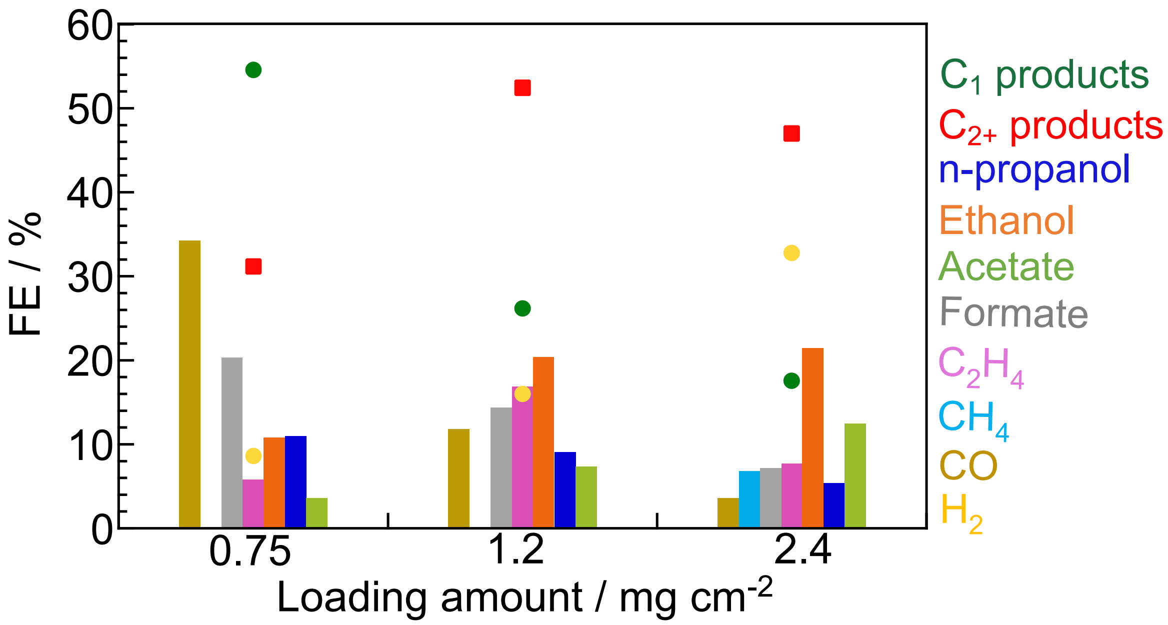

Figure S 18. Effect of catalyst loading on selectivity for CO2R by Eco1-Cu-CO-AR catalyst, in KOH 1 M, CO2 flow rate: 10 ml min-1, applied current density: -100 mA cm^{-2}.

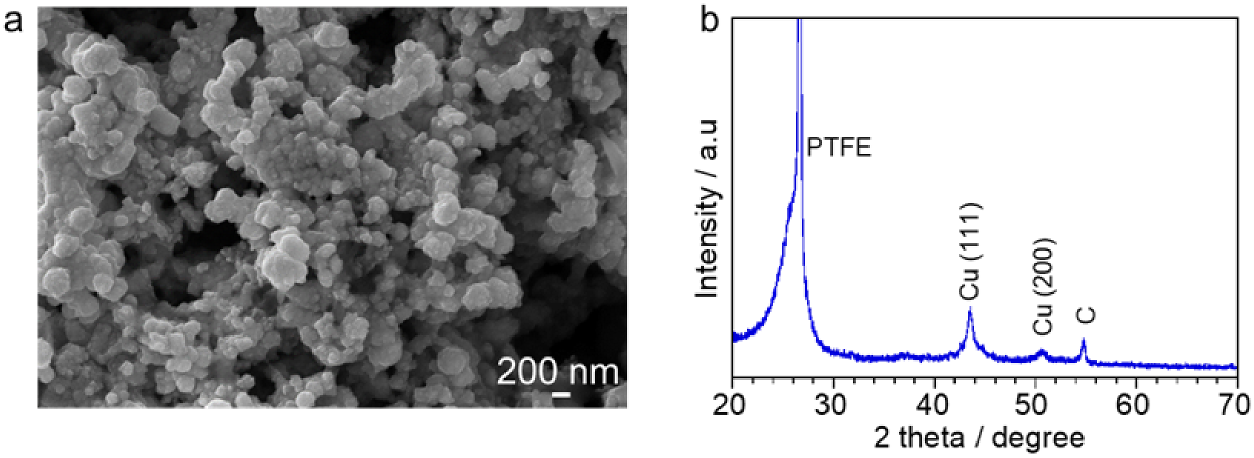

Figure S 19. Post electrolysis characterization of Eco1-Cu-CO-AR catalyst deposited on GDL substrate by SEM (a) and XRD (b). Electrolysis conditions: KOH 1 M, CO2 flow rate: 10 ml min-1, applied current density: -100 mA cm^{-2}.

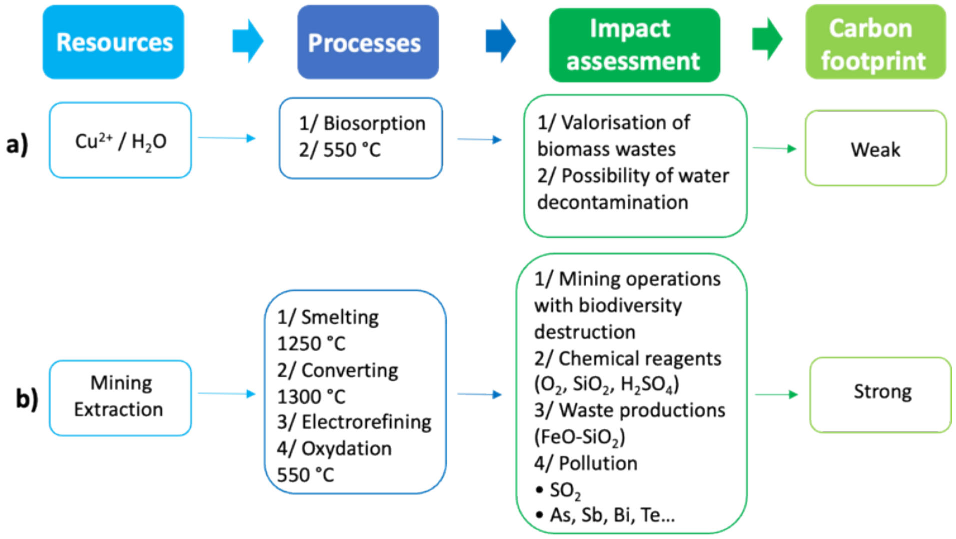

Figure S 20. Qualitative environmental impact assessment of CuO production processes. a) Production process of Eco1-Cu (this work), , b) Conventional production process of CuO (example of pyrometallurgical treatment of chalcopyrite