Supporting Information

Nanostructured Copper-based Electrodes Electrochemically Synthesized on a Carbonaceous Gas Diffusion Membrane with Catalytic Activity for the Electroreduction of CO₂

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Figure S1. SEM image (a) and XRD diffraction pattern (b) of the pristine Toray carbon paper surface



Figure S2. (a) Typical D and G bands referred to the disordered and ordered carbonaceous structure and (b) R values obtained for different pre-treatments



Figure S3. Growth of the metal copper particles over the carbon fiber (17 s passed) Scale bar = $2 \mu m$



Figure S4. SEM images of the thin metal copper deposition over the carbon fiber support. Scale bar = $100 \,\mu m$



Figure S5 - X-ray diffraction pattern of the copper deposit over the fibers



Figure S6. CV study on the Cu 0 /CP electrocatalyst in 0.5 M KOH, scan rate 50 mV s⁻¹, N₂ bubbling. Peaks assigned from a reported study 1



Figure S7. Product distribution obtained during the screening of the applied potentials using the pristine Cu^0/CP electrocatalyst. (a) Productivities of liquid products; (b) productivity of H₂ and (c) detected moles of CO₂ER products

potential (V vs RHE)	electrocatalyst	$\frac{J_{tot}}{(mA\ cm^{-2})}$
-1.1	Cu ⁰	2.20
	Cu ₂ O-Cu ⁰	2.58
	CuOx-Cu ⁰	2.08
	Cu(OH) ₂ -Cu ⁰	2.32
-0.4	Cu ⁰	0.38
	Cu_2O - Cu^0	0.46
	CuOx-Cu ⁰	0.93
	Cu(OH) ₂ -Cu ⁰	0.62

Table S1. Recorded current densities corresponding to the reactions whose product distributions are reported in Figure 5

The total amount of copper electrodeposited over the carbonaceous support was calculated by the Faraday's equation:

Mass of
$$Cu^0 = \frac{(AM)Q}{FZ}$$

where, AM is the atomic mass of Cu (63.546 g mol⁻¹), Q is the total amount of charge passed during the electrodeposition, F is the Faraday's constant (96485 C mol⁻¹) and Z is the number of the exchanged electrons.



Figure S8. Current densities recorded at Cu₂O-Cu⁰/CP electrode during CO₂ER at -0.4 V vs RHE and 0.3 M KHCO₃ as electrolyte after (a) 15 min, (b) 30 min and (c) 1h time of reaction



Figure S9. Recorded current density during 5h reaction using Cu₂O-Cu⁰/CP at -0.4V vs RHE

References

(1) Giri, S. D.; Sarkar, A. Electrochemical Study of Bulk and Monolayer Copper in Alkaline Solution *J. Electrochem. Soc.* **2016**, *163*, H252-H259. doi.org/10.1149/2.0071605jes