Effects of CuO-derived catalysts morphology on carbon dioxide electrochemical reduction in a flow cell

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Supporting Information

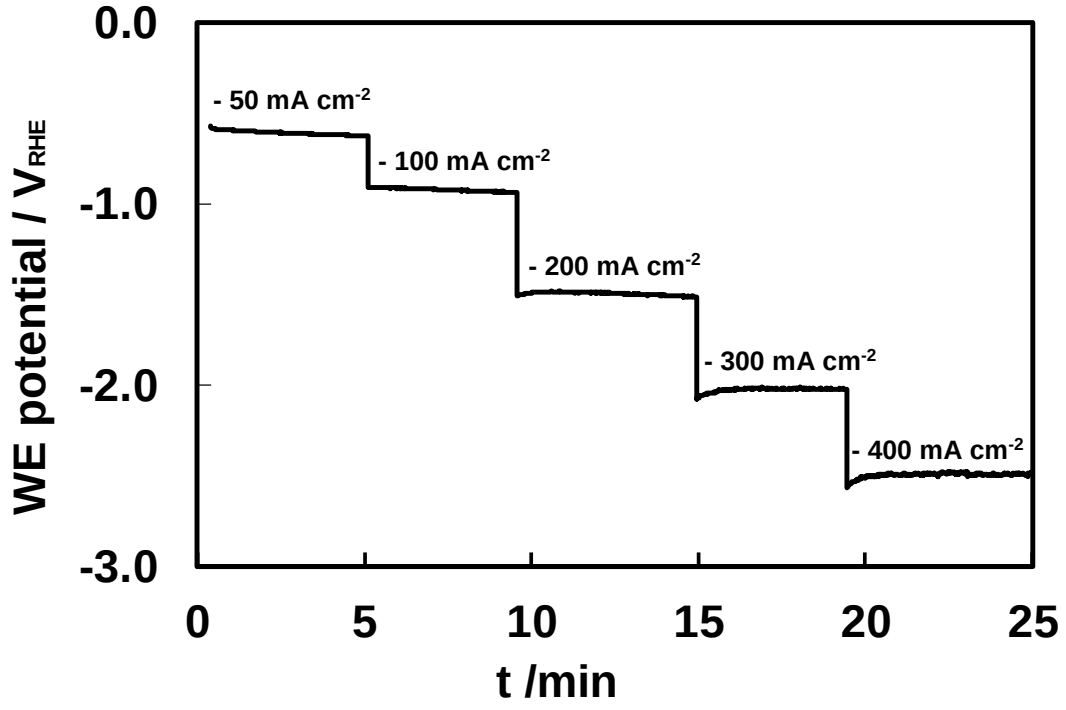

Figure S1. Representation of the standard experiment carried out to investigate the catalytic performance of each GDE towards the electrochemical CO_2 reduction reaction. The working electrode potential vs. Ag/AgCl values have been converted into the RHE scale and are reported as a function of the applied current density.

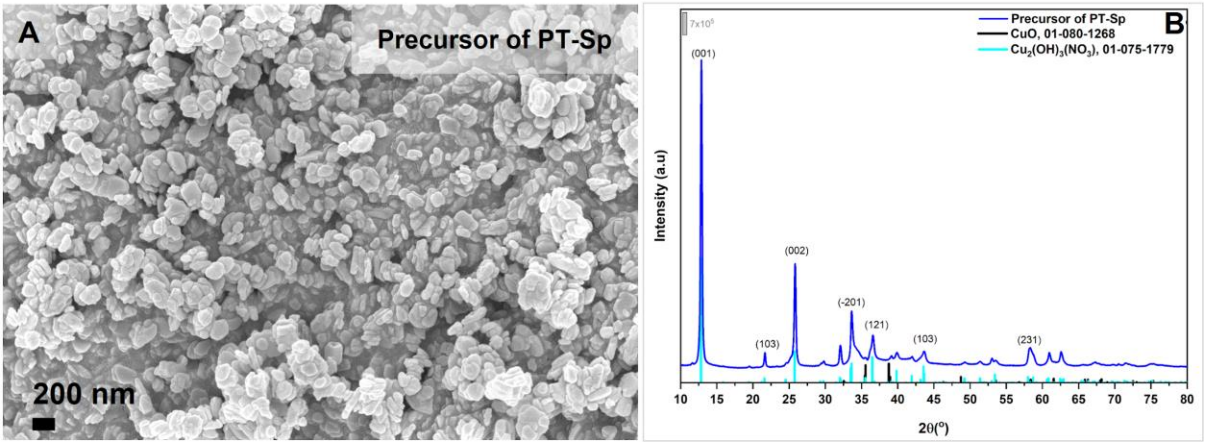

Figure S2. Structural and morphological characterization of the precursor of the PT-Sp sample (*i.e.*, prior than performing the thermal treatment). Panel (a) SEM micrograph of the precursor of PT-Sp sample. Panel (b) XRD pattern of the precursor of the PT-Sp sample (blue). XRD reference patterns: tenorite (CuO, 01-080-1268, black), and copper(II) hydroxide-nitrate ($Cu_2(OH)_3NO_3$, 01-075-1779, cyan).

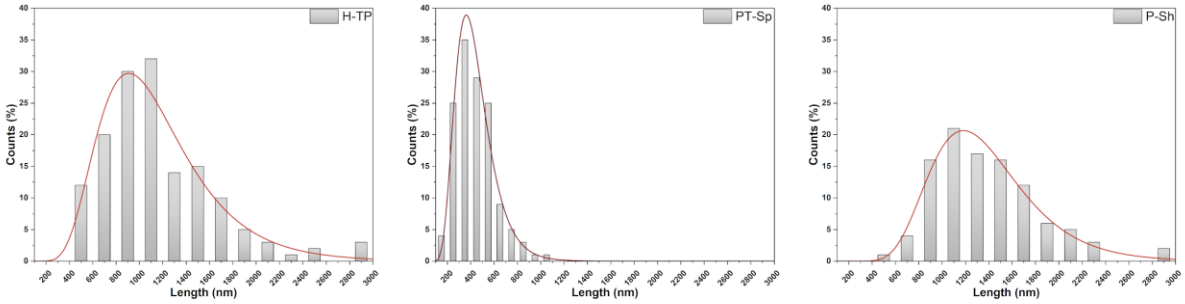

Figure S3. Particle size distribution calculated on the SEM micrographs of the investigated ECs, namely: H-TP sample (hydrothermal route; left), PT-Sp sample (precipitation route with 0.25 M NaOH and thermal treatment; middle), and P-Sh sample (precipitation route with 1 M NaOH; right).

Table S1. Average potential values vs. RHE exhibited by the investigated GDEs at each target current density (between -50 and -400 mA cm^{-2}) during the typical e-CO_2RR test reaction.

SAMPLE	WE potential / V				
	- 50 mA cm^{-2}	- 100 mA cm^{-2}	- 200 mA cm^{-2}	- 300 mA cm^{-2}	- 400 mA cm^{-2}
P-Sh_m	-0.648 ± 0.003	-0.942 ± 0.004	-1.483 ± 0.005	-1.974 ± 0.011	-2.401 ± 0.004
PT-Sp_m	-0.715 ± 0.001	-1.035 ± 0.002	-1.559 ± 0.004	-2.081 ± 0.010	-2.538 ± 0.019
H-TP_m	-0.807 ± 0.100	-1.162 ± 0.002	-1.812 ± 0.015	-2.473 ± 0.059	-3.057 ± 0.125

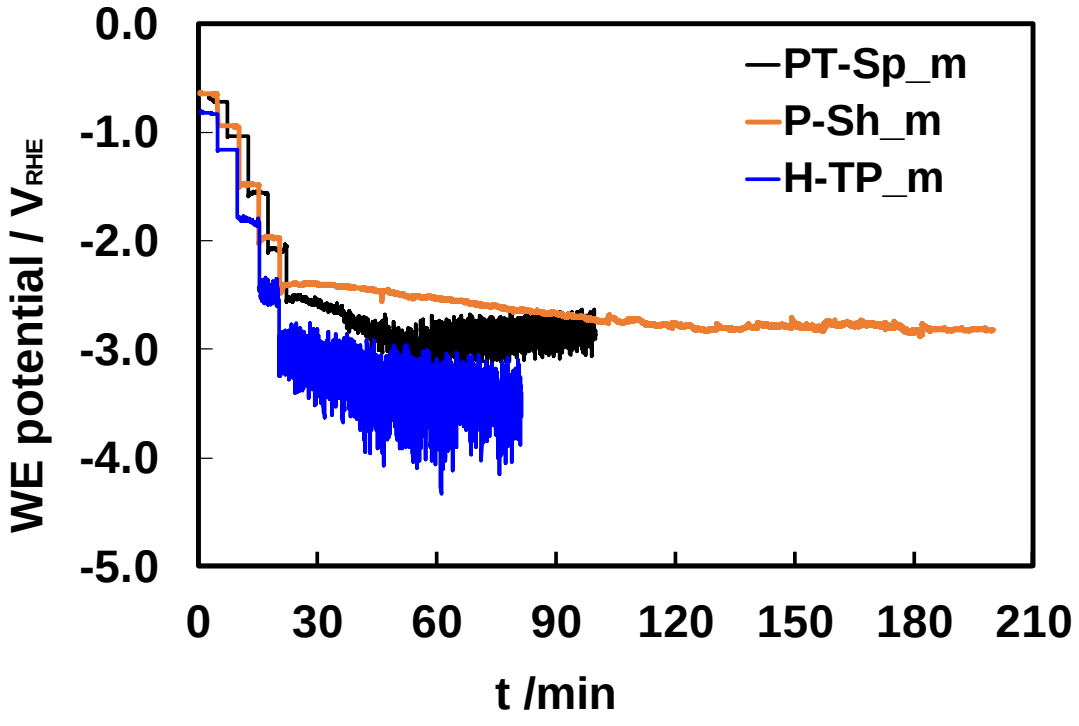

Figure S4. Preliminary stability tests carried out with the electrodes containing a medium loading of CuO pre-catalyst. FE values attained (during these experiments) towards gas products at variable time of the application of the highest absolute value of current density (400 mA cm^{-2}) are collected in Table S2.

Table S2. FE values attained (during the stability tests reported in Fig. S4) towards the main gas products (H_2, CO, CH_4, C_2H_4) with P-Sh_m, PT-Sp_m and H-TP_m electrodes as a function of the application time of the highest absolute value of current density (400 mA cm^{-2}).

P-Sh_m	**FE at -400 mA cm^{-2} (%)**										
	10 min	**20 min**	**30 min**	**40 min**	**60 min**	**80 min**	**90 min**	**120 min**	**140 min**	**160 min**	**180 min**
H_2	13	13	13	13	13	14	14	13	13	13	14
CO	27	25	24	31	30	22	23	19	22	20	15
CH_4	-	-	-	-	-	-	-	-	-	-	-
C_2H_4	42	42	43	42	44	43	44	42	45	46	46

PT-Sp_m	**FE at -400 mA cm^{-2} (%)**					
	10 min	**20 min**	**30 min**	**40 min**	**50 min**	**60 min**
H_2	27	37	52	72	72	85
CO	13	8	4	1	1	1
CH_4	1	-	-	-	-	-
C_2H_4	25	26	14	2	1	1

H-TP_m*	**FE at -400 mA cm^{-2} (%)**					
	10 min	**20 min**	**30 min**	**40 min**	**50 min**	**60 min**
H_2	35	31	31	35	29	28
CO	15	8	6	7	6	3
CH_4	9	8	7	6	5	3
C_2H_4	11	7	7	6	5	4

* *Note*: The underestimation of both the FE towards H_2 and the total FE towards gas products (below 60%) suggests the possible accumulation of H_2 in the catholyte compartment due to the undesired flooding process occurring during the prolonged stability test of the H-TP_m electrode.

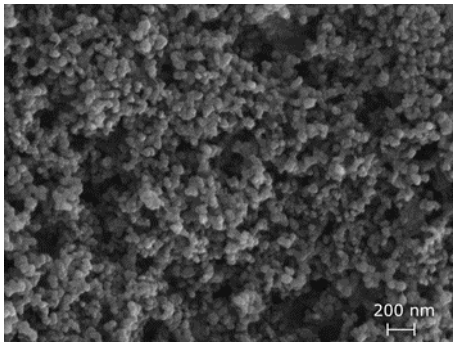

Figure S5. SEM images of the adopted carbon paper.

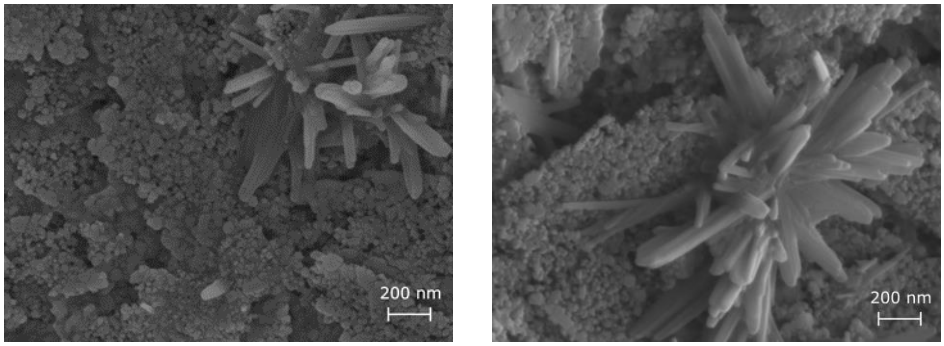

Figure S6. SEM images of the P-Sh_m GDE after performing the e-CO_2RR test.

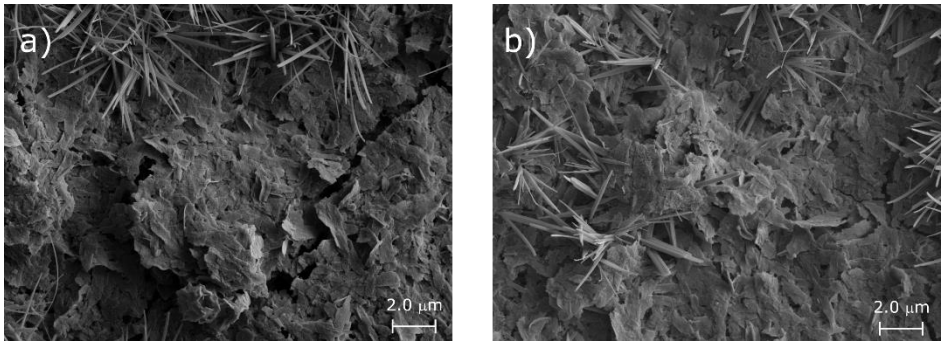

Figure S7. SEM images of the P-Sh_m GDE after performing a prolonged e-CO_2RR test (3 h at -400 mA cm^{-2}).

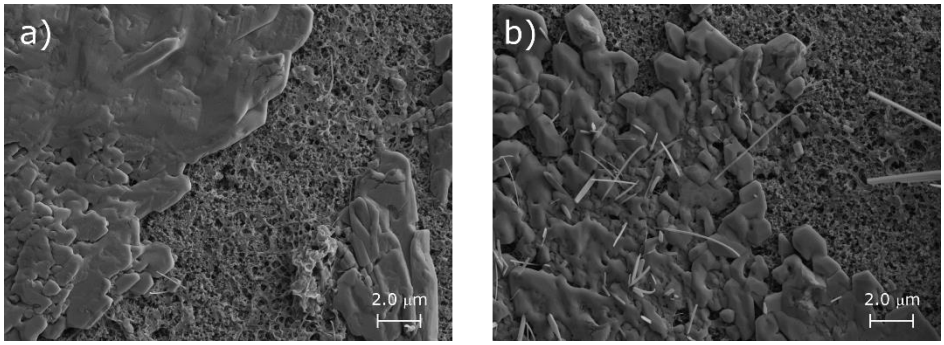

Figure S8. SEM images of the PT-Sp_m GDE after performing the e-CO_2RR stability test (*ca.* 1 h at -400 mA cm^{-2}).

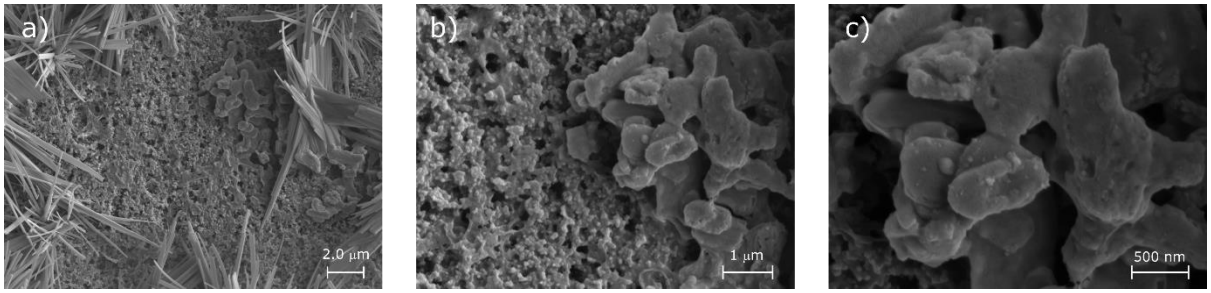

Figure S9. SEM images of the H-TP_m GDE after performing the e-CO_2RR stability test (*ca*. 1 h at -400 mA cm^{-2}).