

## Supporting Information

# CO<sub>2</sub> Electroreduction by Engineering the Cu<sub>2</sub>O/RGO Interphase

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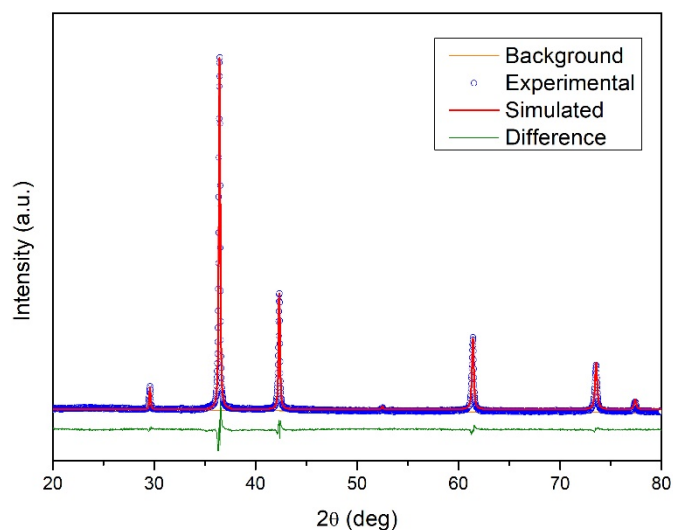
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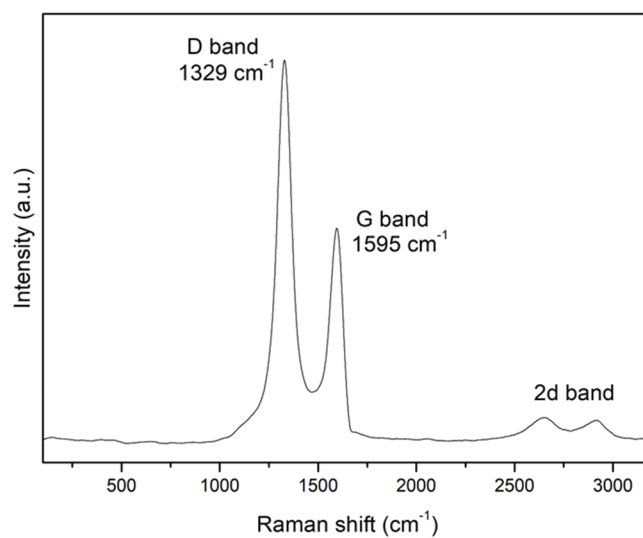
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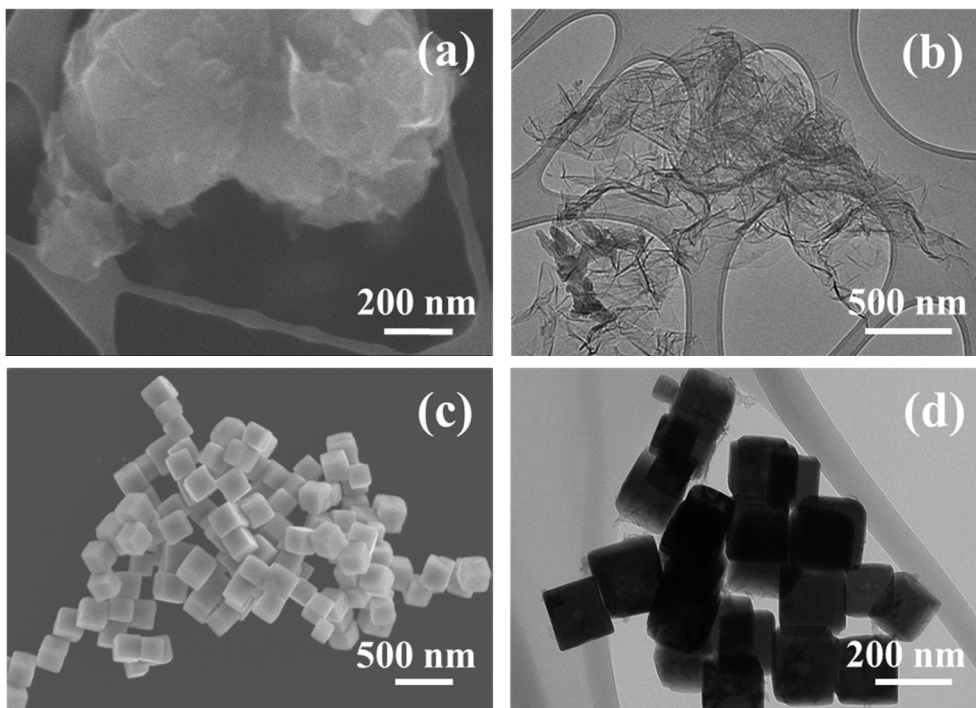
**Figure S1:** Rietveld analysis of the CU Cu<sub>2</sub>O/RGO 2:1 diffractogram.



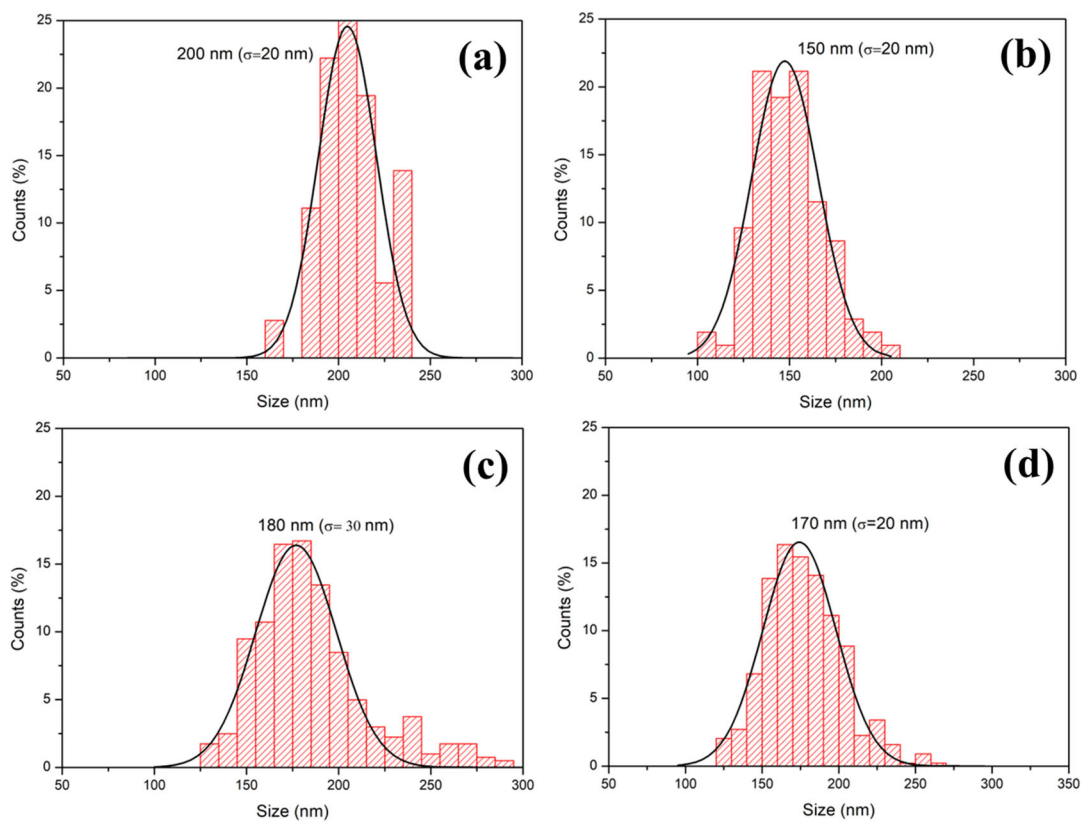
**Figure S2:** Raman Spectrum of pure RGO with the characteristics vibrations.

**Table S1:** Weight fraction of the different CU Cu<sub>2</sub>O/RGO materials from TGA analysis.

Material	%Cu <sub>2</sub> O, theoretical	%Cu <sub>2</sub> O, TGA
CU Cu <sub>2</sub> O/RGO 2:1	66.7%	66.0%
CU Cu <sub>2</sub> O/RGO 1:1	50.0%	46.3%
CU Cu <sub>2</sub> O/RGO 1:2	33.3%	21.3%



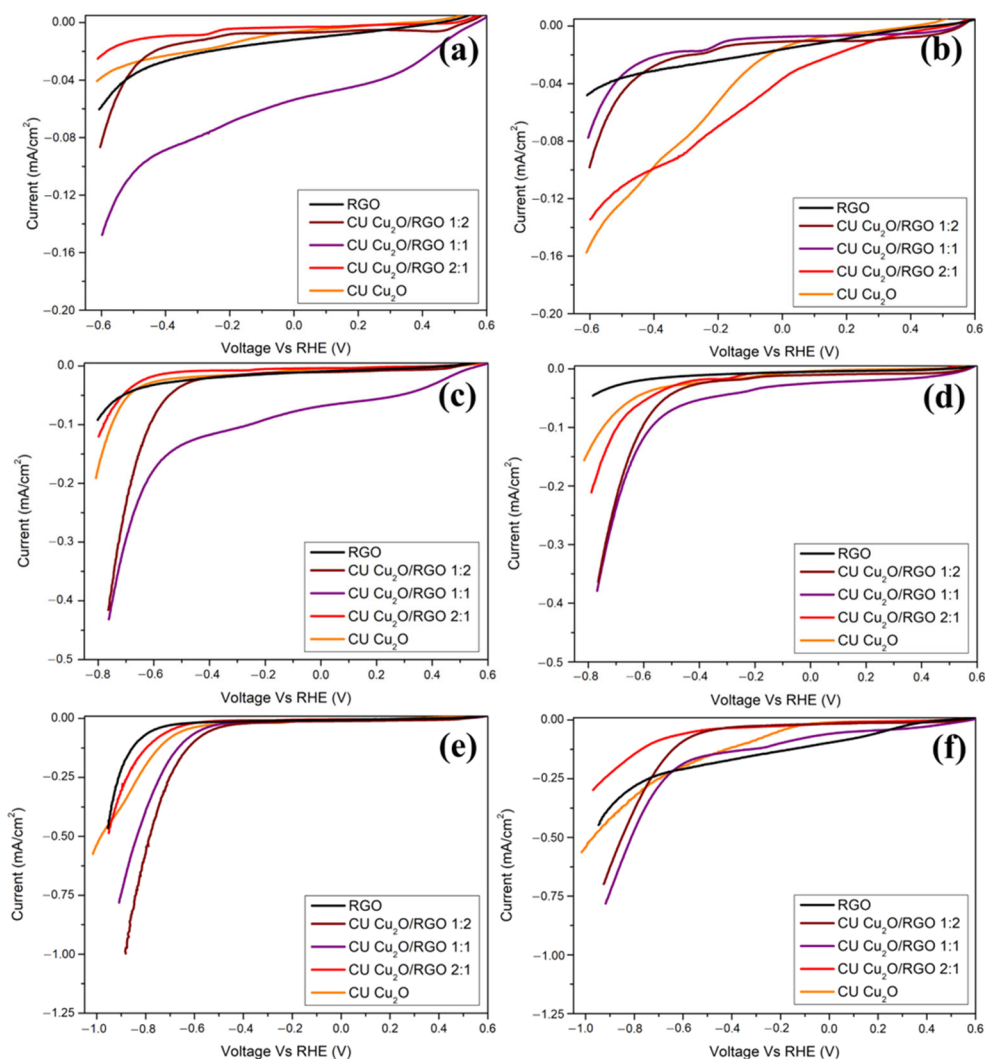
**Figure S3:** (a) SEM and (b) TEM images of pristine RGO. (c) SEM and (d) TEM images of pristine CU  $\text{Cu}_2\text{O}$ .



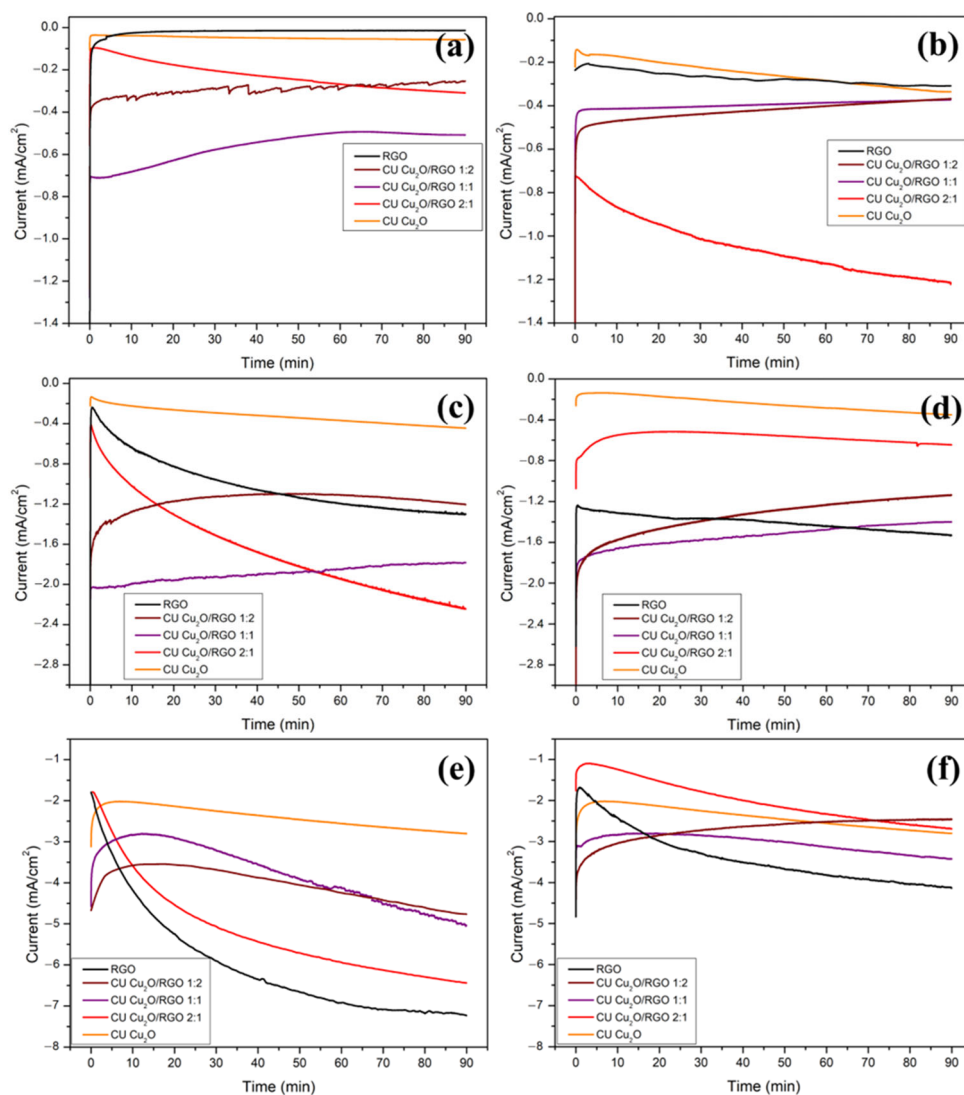
**Figure S4:** Sizes distribution for the different materials (count: 400 particles). (a) CU  $\text{Cu}_2\text{O}$ . (b) CU  $\text{Cu}_2\text{O}/\text{RGO}$  2:1. (c) CU  $\text{Cu}_2\text{O}/\text{RGO}$  1:1. (d) CU  $\text{Cu}_2\text{O}/\text{RGO}$  1:2.

**Table S2:** Size of Cu<sub>2</sub>O nanoparticles on the different materials.

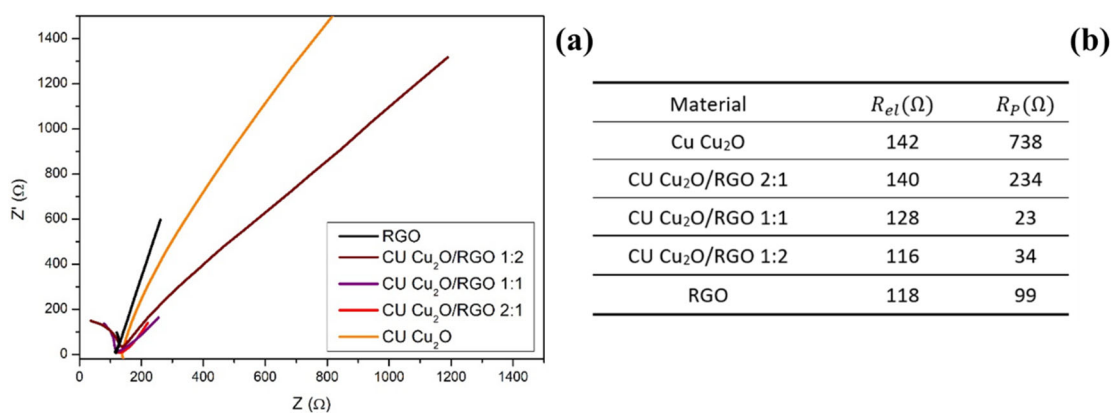
Material	Cu <sub>2</sub> O size (nm)	$\sigma$ (nm)
Cu Cu <sub>2</sub> O	200	20
CU Cu <sub>2</sub> O/RGO 2:1	150	20
CU Cu <sub>2</sub> O/RGO 1:1	180	30
CU Cu <sub>2</sub> O/RGO 1:2	170	20



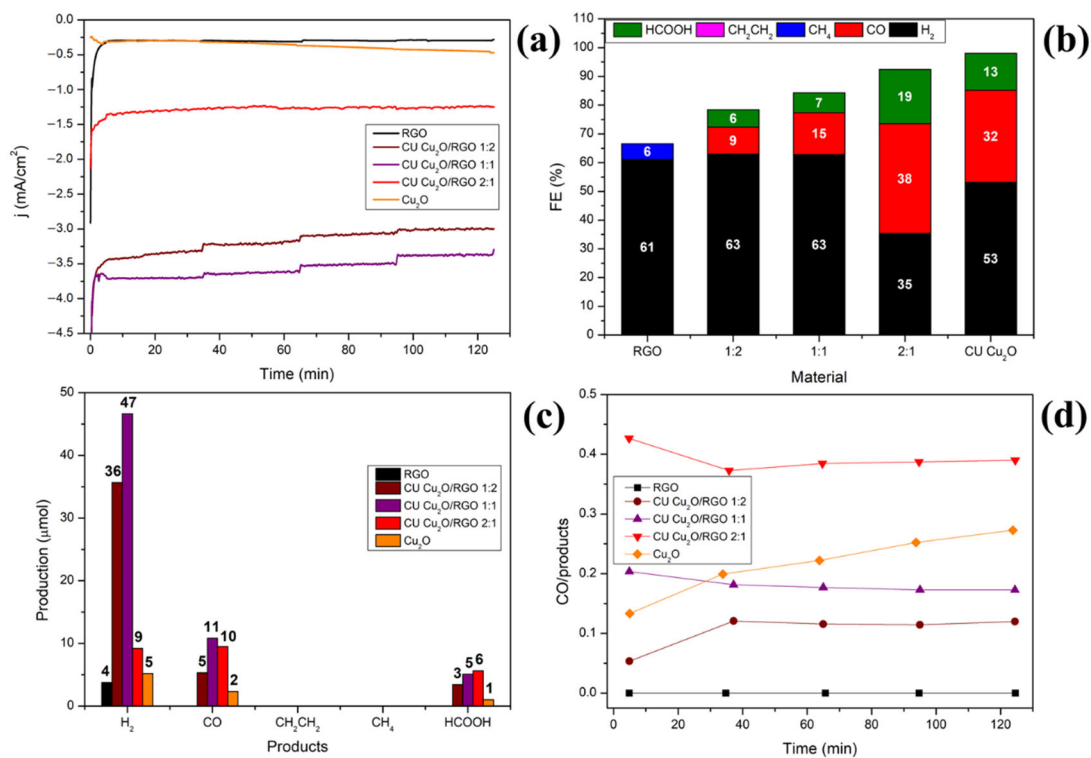
**Figure S5:** Linear sweep voltammeteries at -0.6 V (a and b), -0.8 V (c and d) and -1.0 V (e and f) for the different materials. The measures on the left (a, c and e) were performed in Ar while the measures on the right (b, d and f) were performed in CO<sub>2</sub> atmosphere. All the voltages are vs RHE and corrected with *iR* compensation.



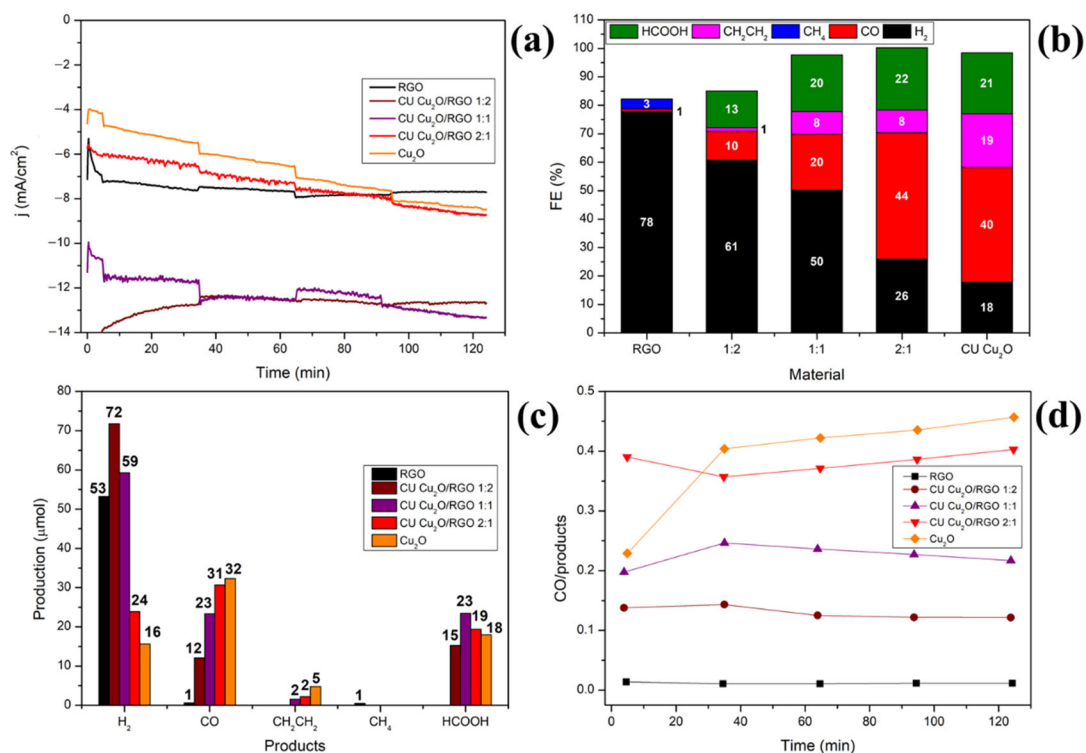
**Figure S6:** Chronoamperometries at -0.6 V (a and b), -0.8 V (c and d) and -1.0 V (e and f) for the different materials. The measures on the left (a, c and e) were performed in Ar while the measures on the right (b, d and f) were performed in CO<sub>2</sub> atmosphere. All the voltages are vs RHE and corrected with iR compensation.



**Figure S7:** A) Nyquist plot at OCV of the different materials performed in CO<sub>2</sub> saturated atmosphere. B)  $R_{el}$  (electrical resistance) and  $R_p$  (polarization resistance) values extrapolated from the simulation of (a) in the frequency range 1000-5000 Hz with a Randle circuit.



**Figure S8:** CO<sub>2</sub>RR tests for the different composites of CU Cu<sub>2</sub>O/RGO at the voltage of  $-0.7$  V vs. RHE. **(a)** Two hour chronoamperometries under saturated CO<sub>2</sub> atmosphere. **(b)** FEs of gaseous and liquid products. **(c)** Products distribution (mmol) of the different compounds after 2 hour chronoamperometries. **(d)** Production profile of CO during the experiment for the different composite materials.



**Figure S9:** CO<sub>2</sub>RR tests for the different composites of CU Cu<sub>2</sub>O/RGO at the voltage of  $-1.1$  V vs. RHE. **(a)** Two hour chronoamperometries under saturated CO<sub>2</sub> atmosphere. **(b)** FEs of gaseous and liquid products. **(c)** Products distribution (mmol) of the different compounds after 2 hour chronoamperometries. **(d)** Production profile of CO during the experiment for the different composite materials.

**Table S3:** Comparison with the literature.

Material	Voltage	Main CO <sub>2</sub> RR product (at the considered voltage)	Reference
CU Cu <sub>2</sub> O/RGO 2:1	$-0.9$ V vs RHE	CO (FE: 50%)	This work
Cu on RGO	$-0.7$ V vs RHE	CO (FE: 20%)	[1]
CU Cu <sub>2</sub> O/N-doped RGO	$-1.1$ V vs RHE	CO (FE: $\approx 10\%$ )	[2]
CoTMPyP on RGO	$-0.7$ V vs RHE	CO (FE: 45%)	[3]
R-ZnO/RGO	$-0.7$ V vs RHE	CO (FE: $\approx 70\%$ )	[4]
Bi-RGO	$-0.75$ V vs RHE	HCOO <sup>-</sup> (FE: 60%)	[5]

**Table S4:** ECSA obtained for the different materials.

Material	ECSA (cm <sup>2</sup> )
Cu Cu <sub>2</sub> O	0.22
CU Cu <sub>2</sub> O/RGO 2:1	0.56
CU Cu <sub>2</sub> O/RGO 1:1	1.65
CU Cu <sub>2</sub> O/RGO 1:2	1.66
RGO	0.90

The procedure to obtain ECSA values follow the reference [6].

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