

SUPPORTING INFORMATION

Electrocatalytic reduction of CO₂ over dendritic-type Cu- and Fe-based electrodes prepared by electrodeposition

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S1. Weight, Porosity and Effective Area

Cu-CF₂

For the electrocatalysts forming leafy dendrite-like structures (as observed in the SEM view of **Figure S1**), the actual weight measured by peeling the electrode from the metal base was about 25-30 mg, indicating 50 % porosity of the electrode. The electrode surface area per geometrical electrode area (1 cm²) is 19 cm².

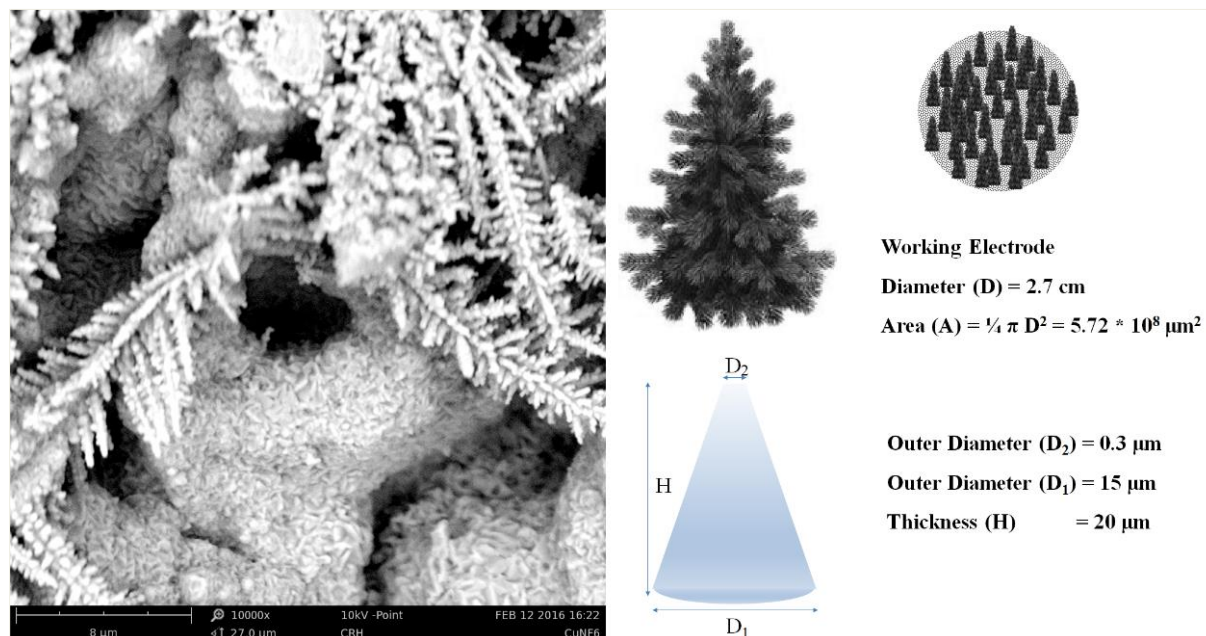


Figure S1: SEM image of Cu-CF₂ and schematic depiction of the porous structure.

Figure S2 shows a SEM image of Cu-GDL_{0.5}. A schematic depiction of the truncated conical hollow structures, evidencing many intra-porous structures in the nanofoam, has also been reported. The NFs have about 84 % porosity and a surface area of about 38 cm² (per 1 cm² geometrical area).

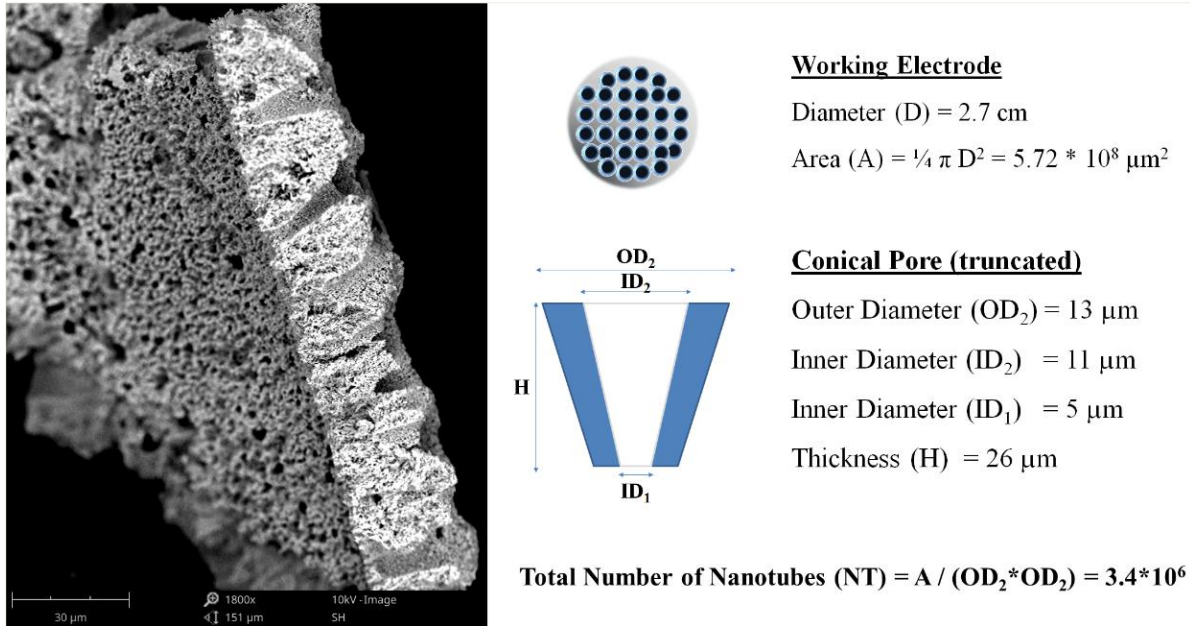
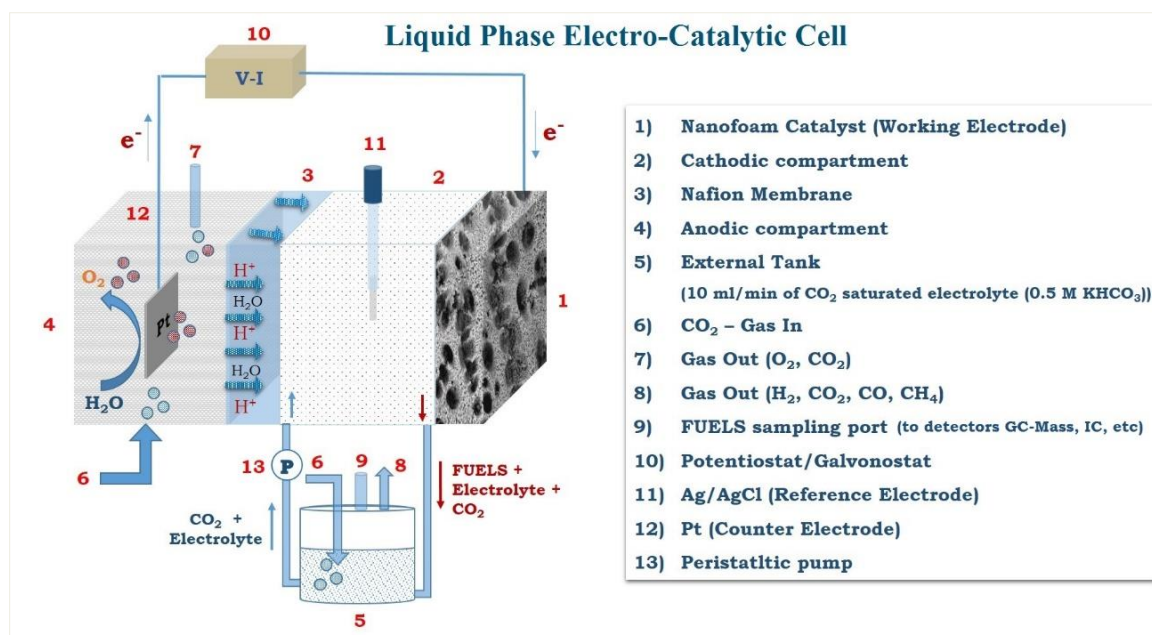


Figure S2: SEM Image of Cu-GDL_{0.5} and schematic depiction of the porous structure.

S2. Electrocatalytic device for CO₂ reduction.



Scheme S1: Scheme of the experimental apparatus for the CO₂ electro-reduction.

S3. SEM characterization

Figure S3 shows: a) Fe-AG₂ and b) Fe-GDL_{0.5}. These samples are highly dense, evidencing very small hollow structures of 50-100 nm.

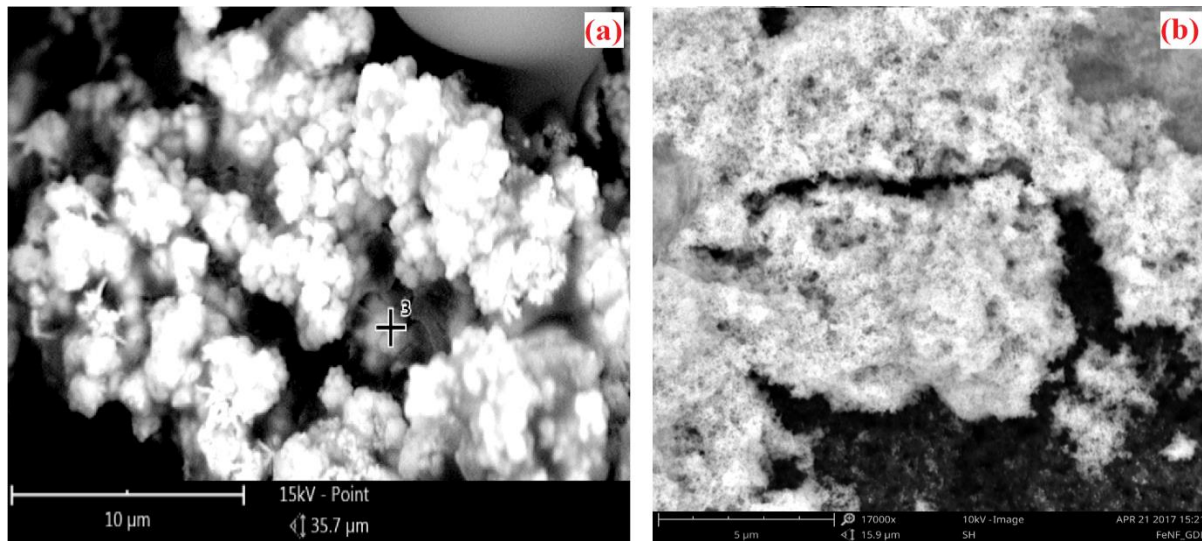


Figure S3: SEM images of a) Fe-AG₂ and b) Fe-GDL_{0.5}.

Figure S4a shows SEM image of Fe(II)-Ti, which evidence a very dense and thick dendrite structure, confirming that the Fe NFs become thicker and less porous by increasing time of electro-deposition.

Figure S4b shows SEM image of Fe(III)-Ti, which evidence a holey structure.

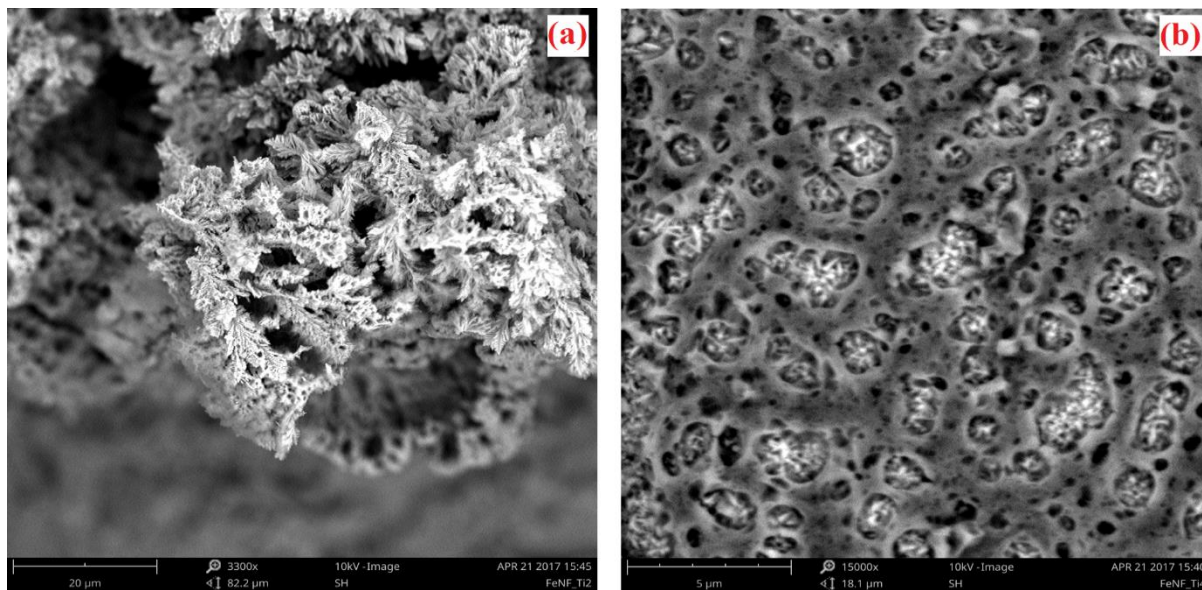


Figure S4: SEM images of a) Fe(II)-Ti and b) Fe(III)-Ti, both 30 s electrodeposition.

However, for longer electrodeposition time ($t = 90$ s), a more open and clear holey structure can be observed for Fe(III)-Ti (see **Figure S5**).

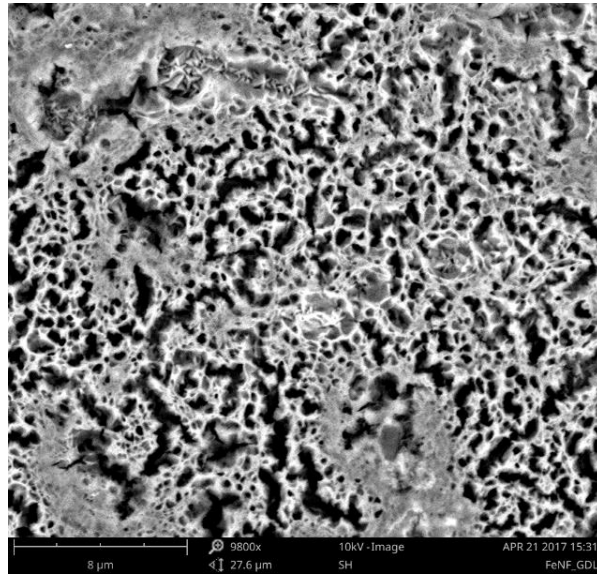


Figure S5: SEM image of Fe(III)-Ti (90 s electrodeposition time).

S4. EDX Analysis

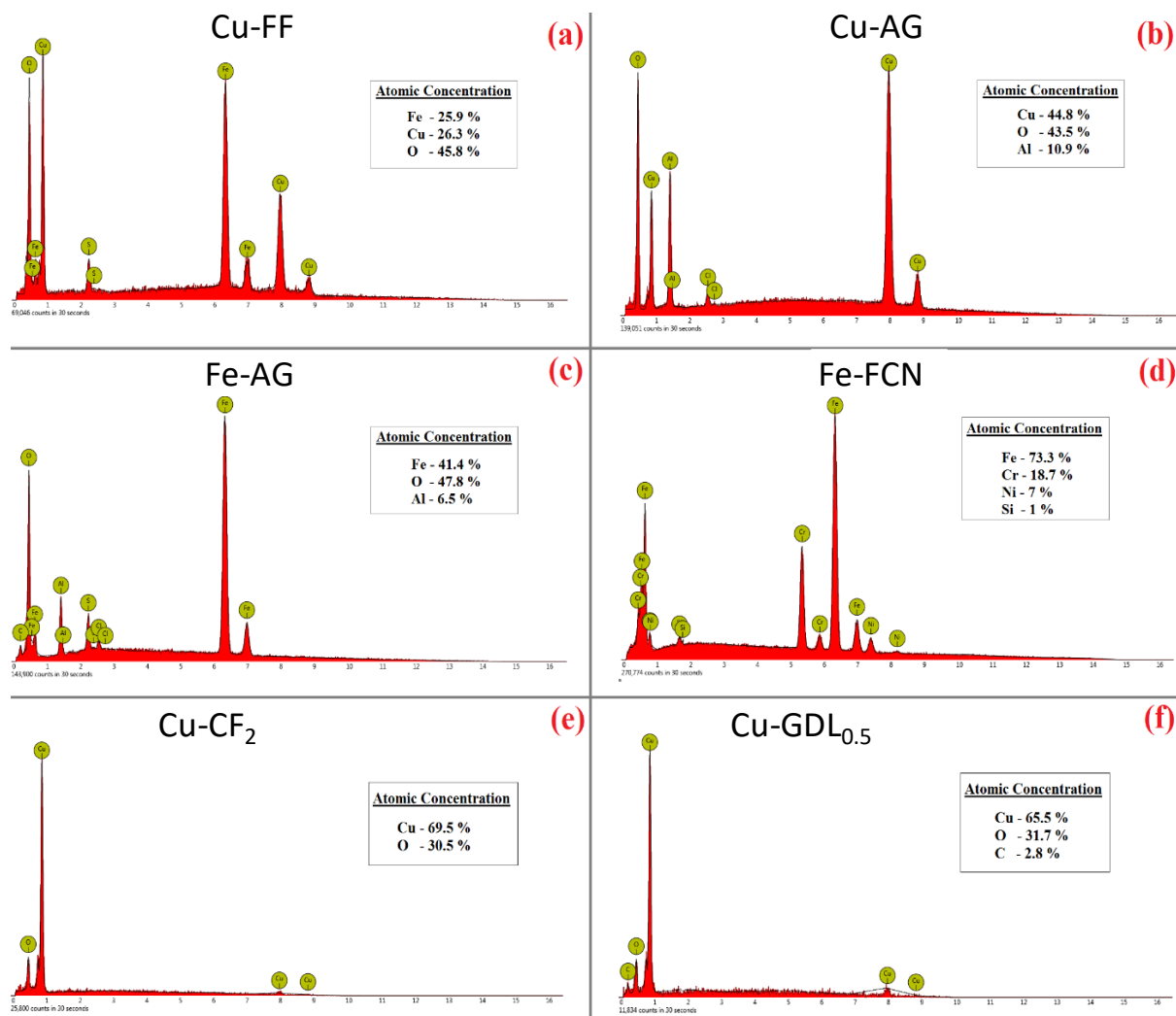


Figure S6: EDX of different Cu- and Fe-based electrodes.

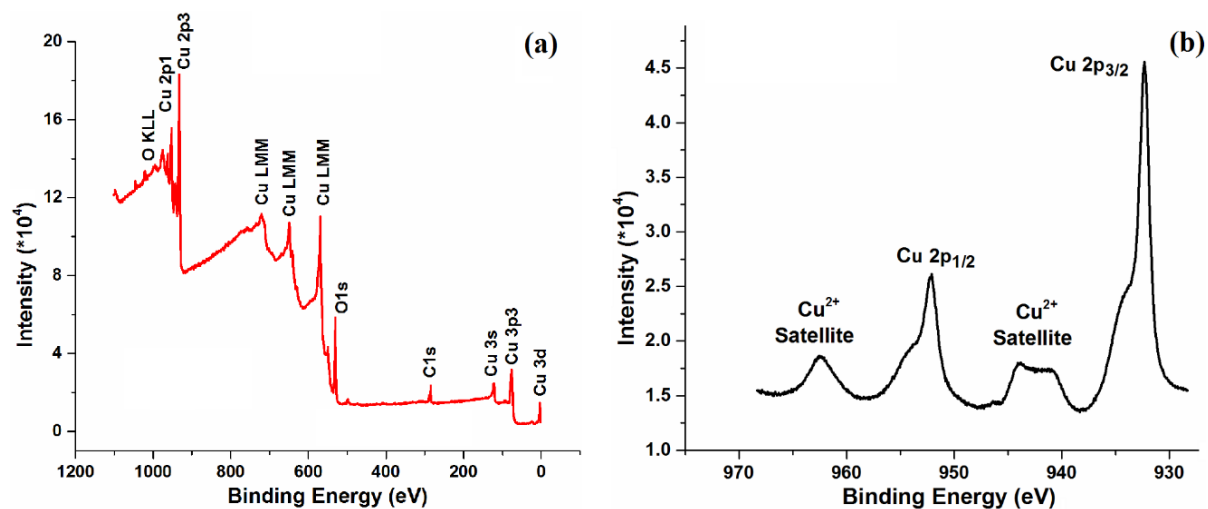


Figure S7: a) XPS wide scan survey of Cu-CF and b) high-resolution spectra of the Cu 2p doublets.

The C-1s binding energy of adventitious carbon (284.9) was used as the reference.

S6. Electrocatalytic tests

Table S1: Production rates of Cu and Fe electrocatalysts in the CO₂ electro-catalytic reduction at the applied potential of -1.5 V (vs. Ag/AgCl).

CATALYSTS	PRODUCTS ($\mu\text{mol}\cdot\text{h}^{-1}$)									
	<i>Formic Acid</i>	<i>Acetic Acid</i>	<i>Methanol</i>	<i>Acetone</i>	<i>Iso-Propanol</i>	<i>Ethanol</i>	<i>CH₄</i>	<i>CO</i>	<i>H₂</i>	<i>C-Products (NET)</i>
Bare Substrate										
<i>Cu Foil</i>	12.5	0.06	0.37	0.01	0.01	0.02	2.07	2.80	264.5	17.8
<i>Fe-Cr-Ni Foil</i>	0.12	0.00	-	-	-	-	-	-	22.8	0.12
<i>Al Foil</i>	0.58	0.00	-	-	-	-	-	-	89.3	0.58
<i>Fe Foil</i>	0.16	0.00	-	-	-	-	-	-	57.2	0.16
With Cu or Fe electrodeposited										
<i>Cu-CF₁</i>	1.96	0.07	-	-	-	-	-	-	97.8	2.03
<i>Cu-CF₂</i>	7.87	0.28	0.03	-	0.06	0.05	2.24	11.5	1069.6	22.0
<i>Cu-CF₄</i>	6.16	0.14	0.03	-	-	0.02	-	-	340.9	6.35
<i>Cu-FCN</i>	23.6	0.26	0.84	0.01	-	0.01	-	19.9	777.9	44.6
<i>Cu-AG</i>	11.0	6.43	0.29	0.01	-	0.01	-	3.30	226.6	21.1
<i>Cu-FF</i>	0.16	0.42	0.37	-	-	-	2.25	2.13	61.6	5.33
<i>Fe-FCN</i>	5.31	0.63	0.62	-	0.01	0.02	-	-	1538.0	6.59
<i>Fe-AG</i>	0.36	0.82	0.07	-	-	-	-	-	480.3	1.25

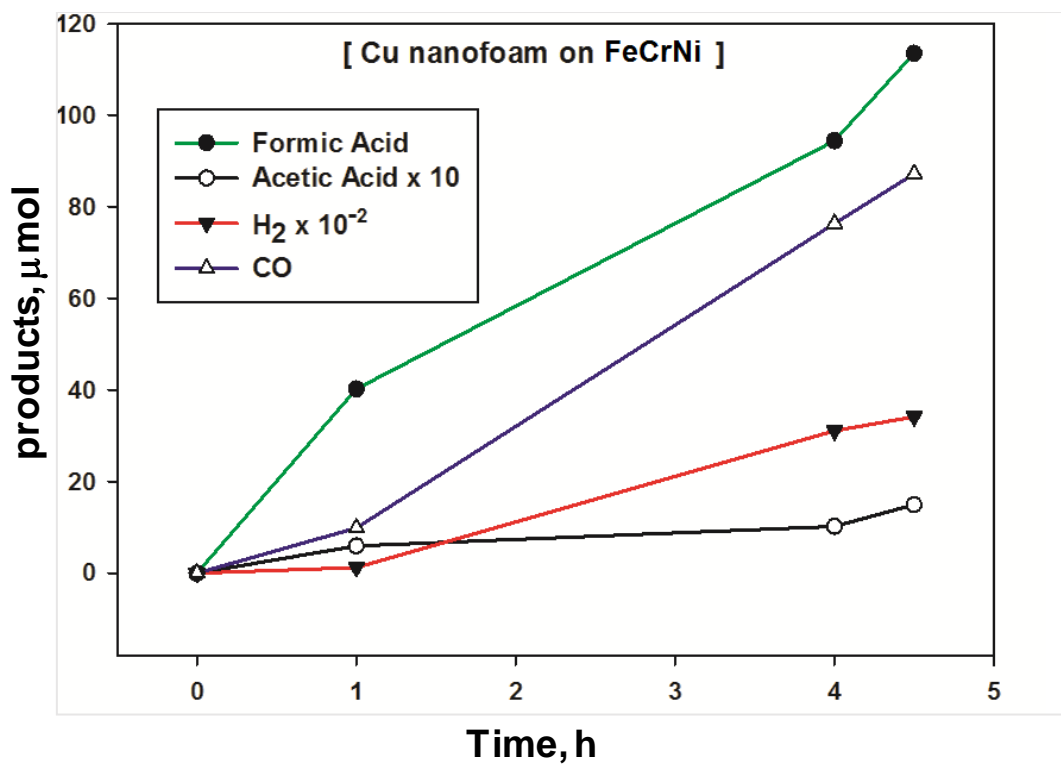


Figure S8: Productivity to formic acid, acetic acid, CO and H₂ for Cu-FCN.