

## SUPPORTING INFORMATION

### **Using copper-based biocathodes to improve carbon dioxide conversion efficiency into methane in microbial methanogenesis cells**

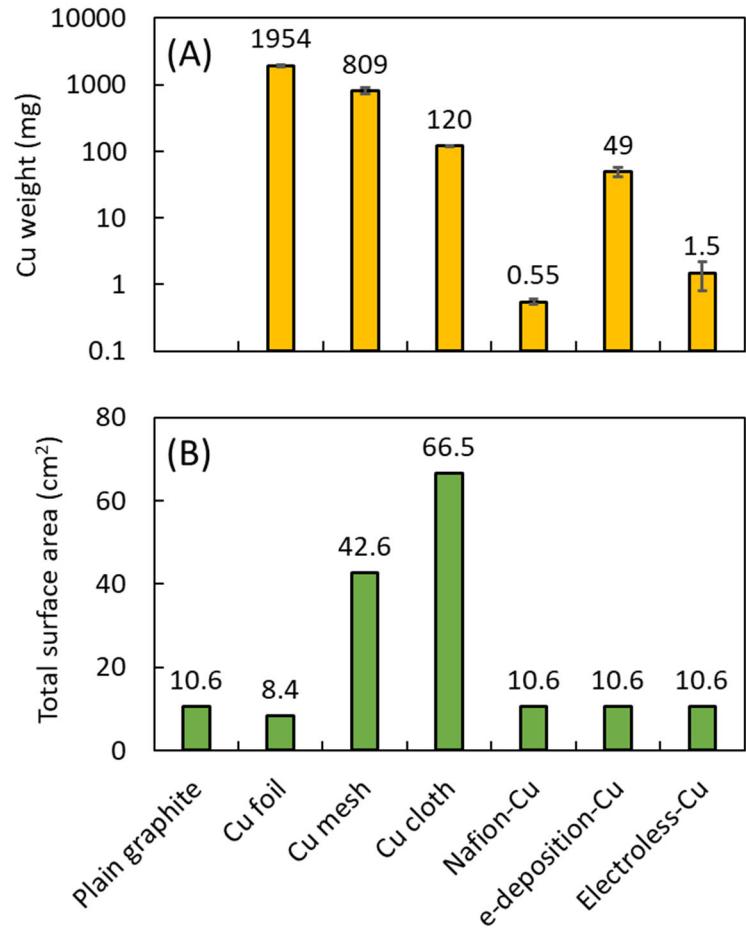
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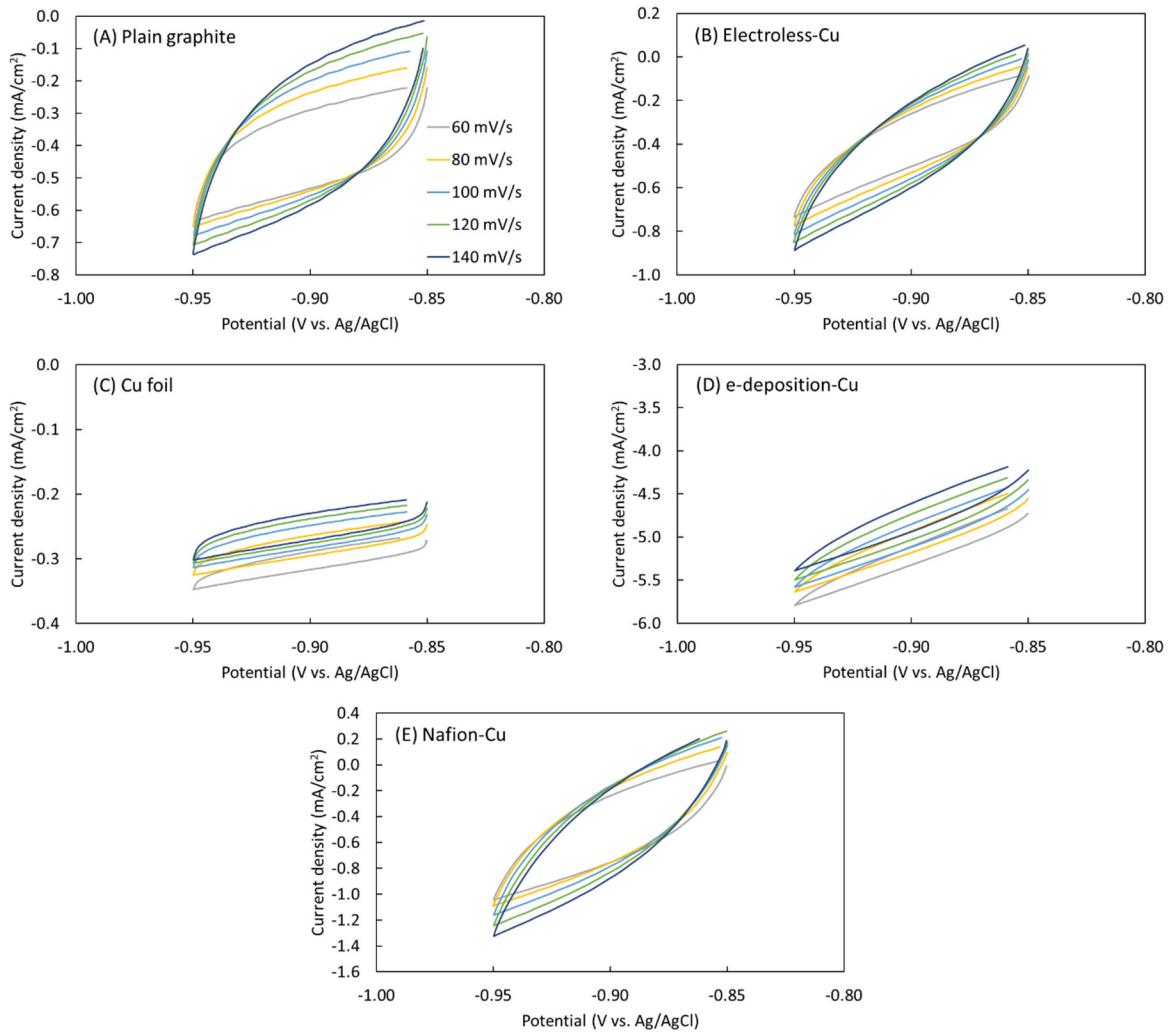
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**Table S1.** Comparison with previous MMC studies.

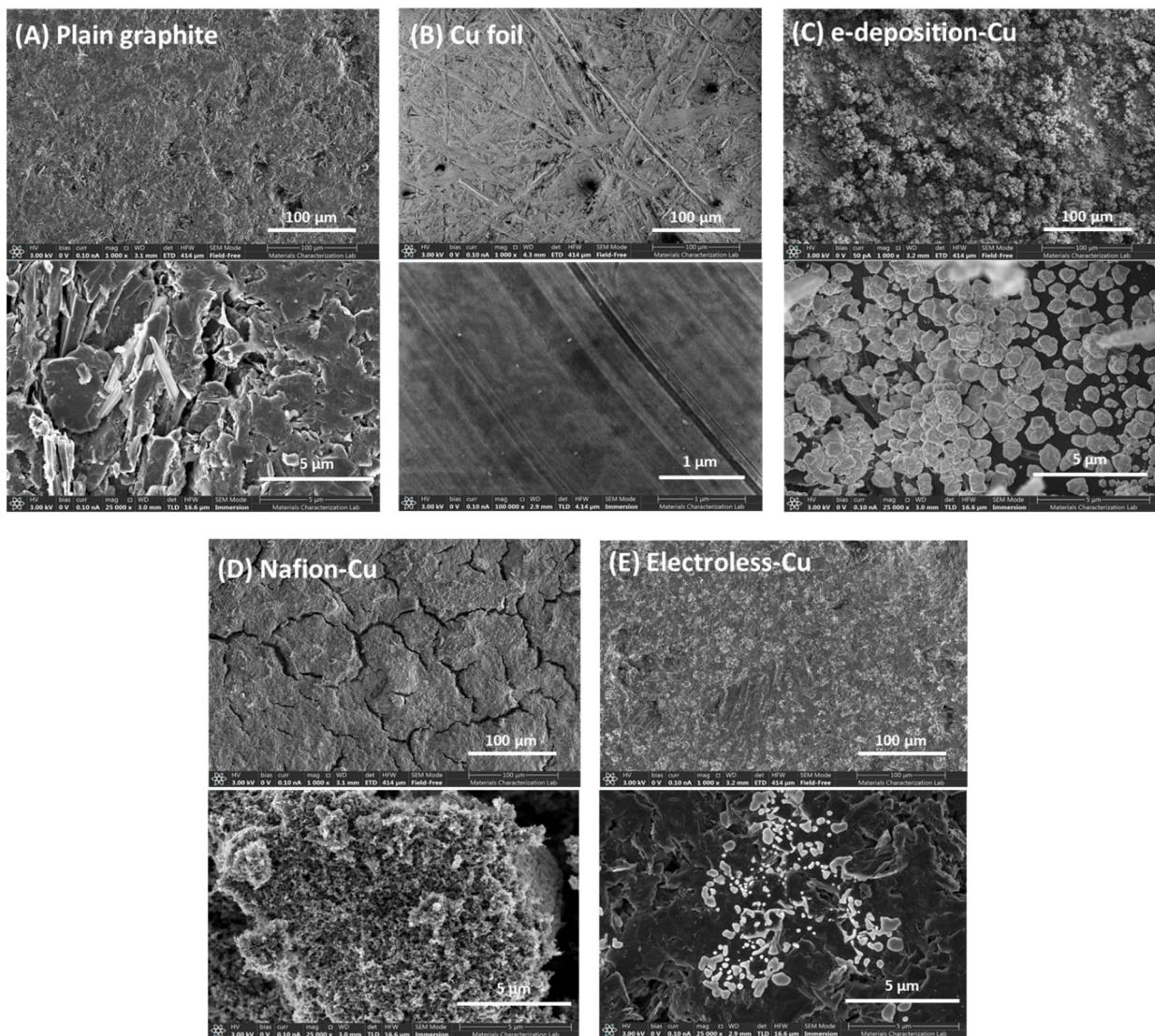
Anode material	Cathode material	Cathodic potential (V vs. Ag/AgCl)	Methane production rate (L/L/d)	Cathodic methane recovery (%)	Ref
Ti/ IrO <sub>2</sub> –Ta <sub>2</sub> O <sub>5</sub>	GGAC (Ti plate)	-1.05	4.6	27	[1]
Pt/Ti/IrO <sub>2</sub>	GAC	-0.58	4.3	66	[2]
Pt/Ti/IrO <sub>2</sub>	Graphite granules	-1.1	4.1	67	[2]
Ti/IrO <sub>2</sub>	Ti mesh/Pt	-2.5	1.6	65	[3]
Ti/IrO <sub>2</sub>	Ti mesh/Pt	-2.1	1.6	95	[3]
Ti/IrO <sub>2</sub>	Ti mesh/Pt	-1.84	1.6	85	[4]
Ti/IrO <sub>2</sub>	Ti mesh/Pt	-1.6	1.4	62	[3]
Ti/ IrO <sub>2</sub> –Ta <sub>2</sub> O <sub>5</sub>	GGAC (Ti plate)	-1	1.0	22	[1]
Pt/Ti	Graphite felt	-0.9	0.5	73	[5]
Pt foil	Graphite felt	-1.3	0.4	69	[6]
Ti/ IrO <sub>2</sub> –Ta <sub>2</sub> O <sub>5</sub>	Ni foam	-0.95	0.3	93	[7]
Carbon felt	Carbon felt	-0.75	0.2	89	[8]
Graphite felt	Graphite felt	-0.9	0.1	99	[9]
Graphite felt	Graphite felt	-0.8	0.07	92	[9]
Carbon brush	Carbon cloth	-1	0.03	96	[10]
Carbon fiber brush	Carbon cloth	-1	0.02	36	[11]
Glassy carbon rod	Carbon paper	-0.95	0.007	76	[12]
Carbon brush	Pt/GB	-0.6	0.006	78	[13]
Carbon cloth	Carbon cloth	-0.7	0.005	93	[14]
Pt/Ti	Graphite felt	-0.75	0.005	18	[15]
Carbon brush	Graphite block	-0.9	0	0	This study
Carbon brush	Cu foil	-0.9	0	0	This study
Carbon brush	e-deposition-Cu	-0.9	0.001	28	This study
Carbon brush	Nafion-Cu	-0.9	0.0002	13	This study
Carbon brush	Electroless-Cu	-0.9	0.003	22	This study



**Fig. S1.** (A) Total mass of copper and (B) total surface area of each electrode.



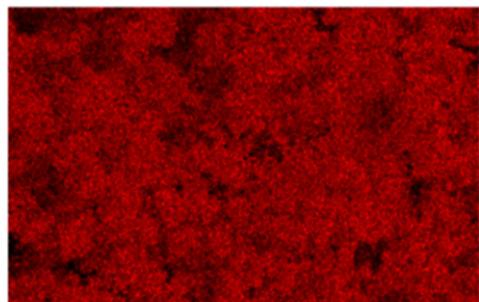
**Fig. S2.** Cyclic voltammetry (CV) curves using different cathode materials to calculate electrochemical double-layer capacitance ( $C_{dl}$ ) and estimate electrochemically active surface area.



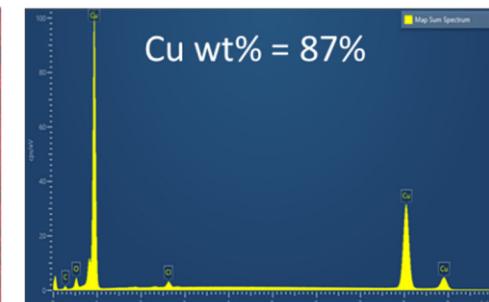
**Fig. S3.** Scanning electron microscopic (SEM) images of the surface of each cathode materials.

(A) e-deposition-Cu

Cu K $\alpha$ 1

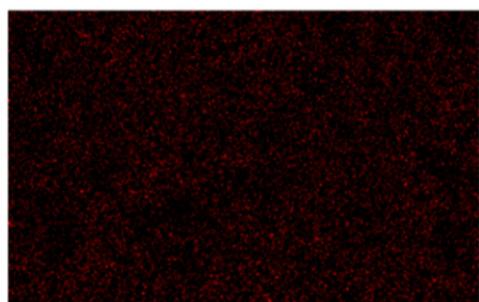


100μm

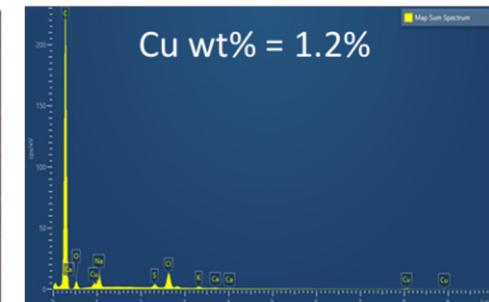


(B) Electroless-Cu

Cu K $\alpha$ 1

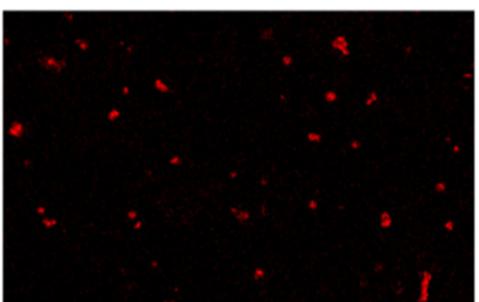


100μm

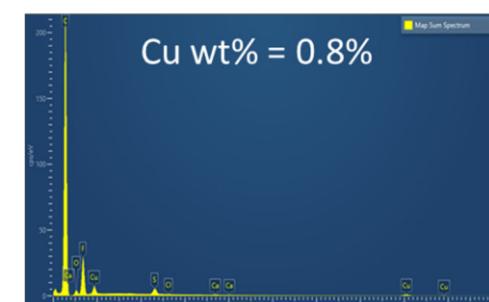


(C) Nafion-Cu

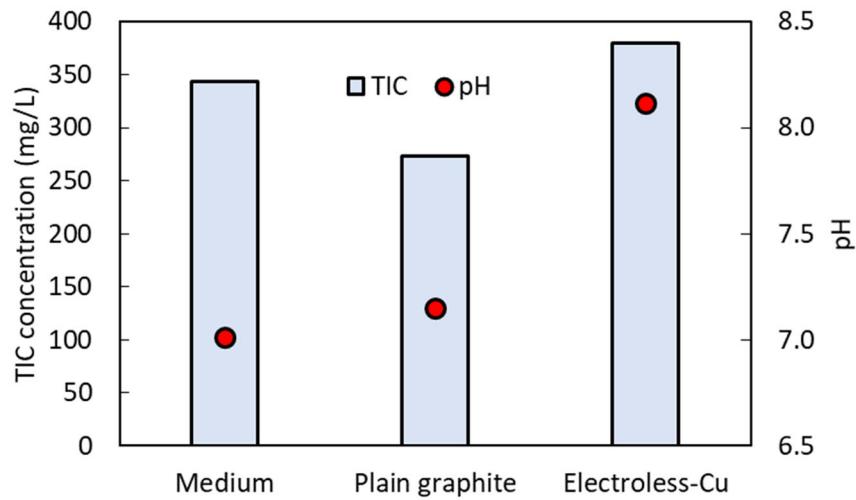
Cu K $\alpha$ 1



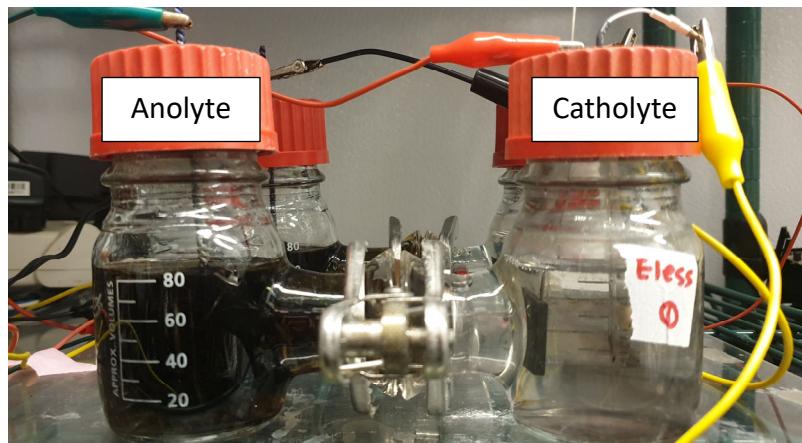
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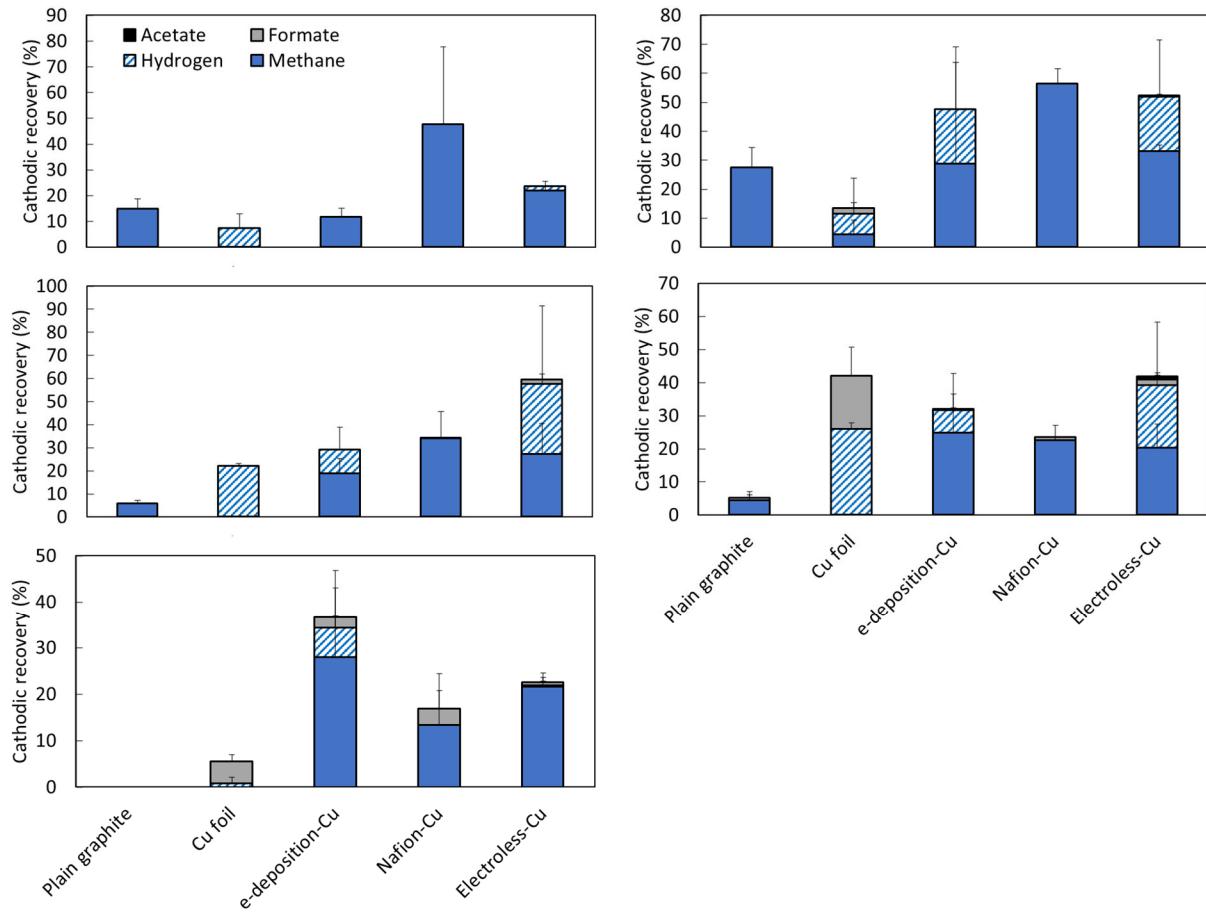
**Fig. S4.** Energy-dispersive X-ray spectroscopy (EDS) mapping results for the cooper-based cathode materials prepared by different coating methods. Atomic percentage of copper was calculated based on the EDS spectrum.



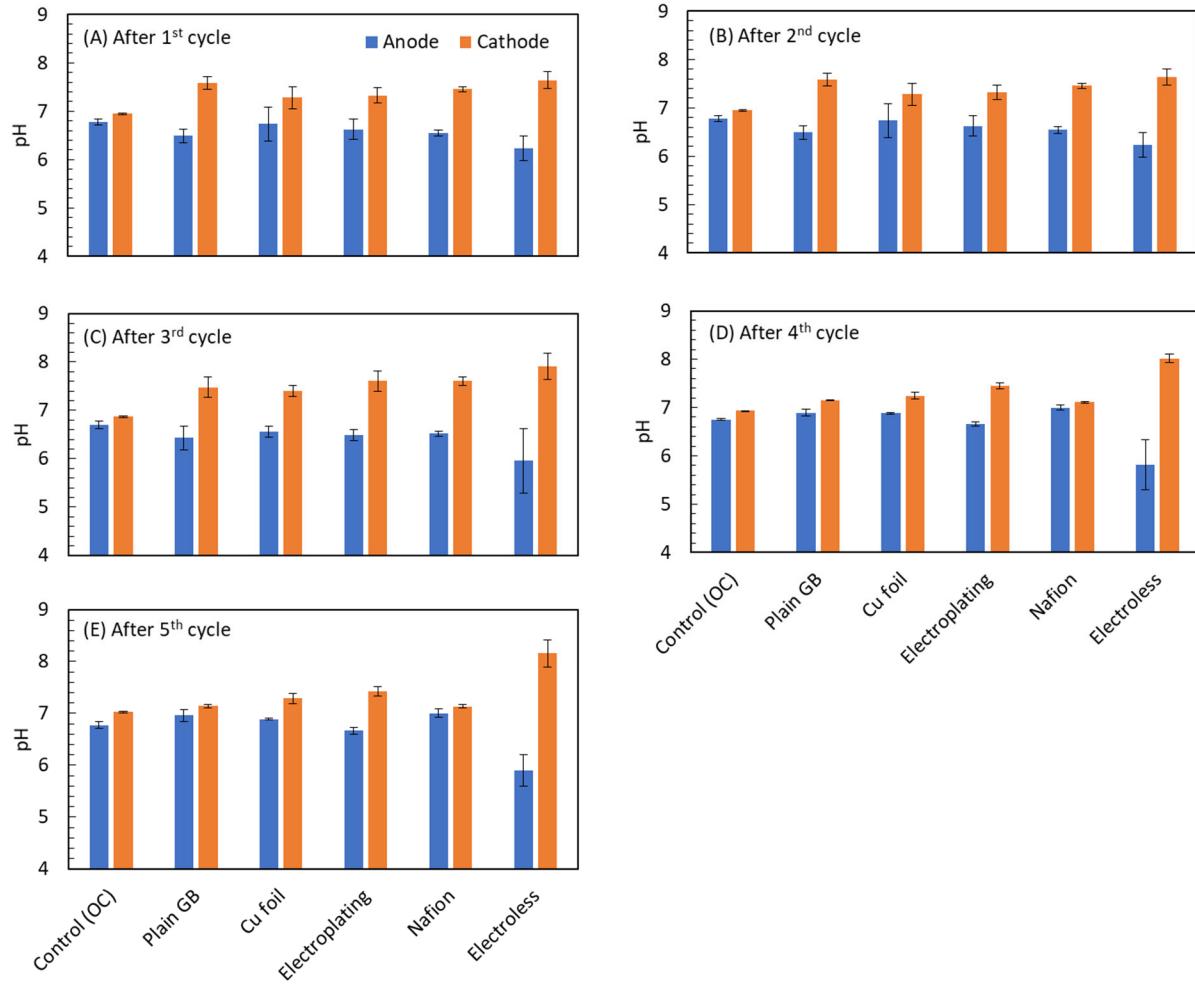
**Fig. S5.** Changes in pH and TIC concentration after 24 hours of abiotic reaction.



**Fig. S6.** Change in the anolyte color of electroless-Cu reactors after the fifth cycle.



**Fig. S7.** Cathodic recovery based on biogas and VFA productions at the end of each cycle



**Fig. S8.** pH of anolyte and catholyte at the end of each cycle

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