Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Electricity-saving H_2 Production from Hybrid Acid/Alkali Electrolyzer Assisted by Anodic Glycerol Oxidation

Bowen Liu[a], Genxiang Wang[b], Xin Feng[a], Ling Dai[a], Zhenhai Wen[a,b*], Suqin Ci[a*]

[a]*Key Laboratory of Jiangxi Province for Persistent Pollutants Control, National-Local Joint Engineering Research Center of Heavy Metals Pollutants Control and Resource Utilization and Resources Recycle, Nanchang Hangkong University, Nanchang 330063, Jiangxi, China.*

[b]*CAS Key Laboratory of Design and Assembly of Functional Nanostructures, and Fujian Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China.*

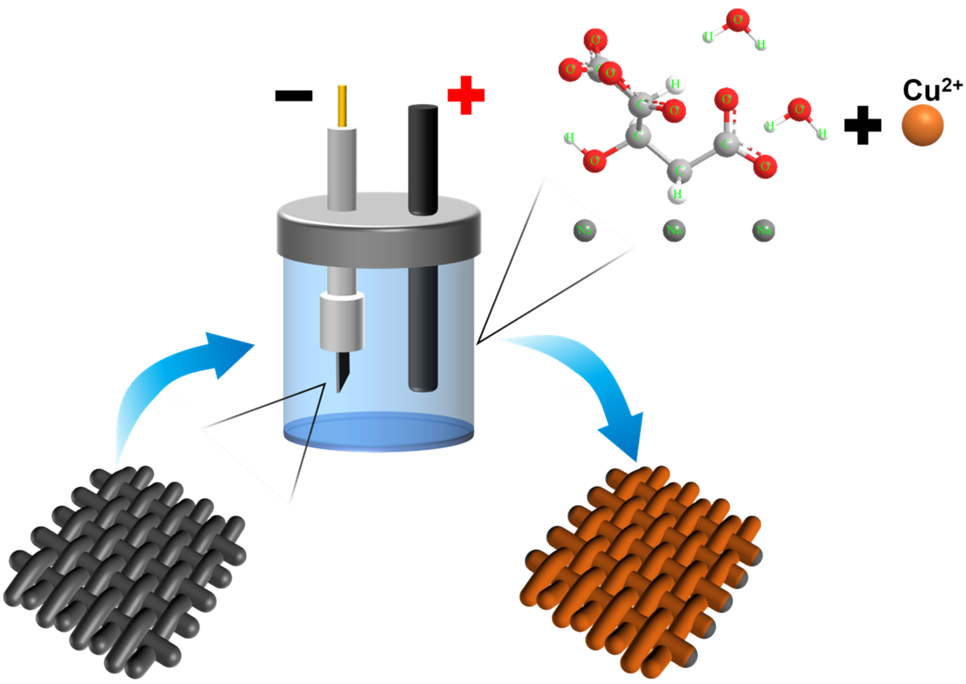

Fig. S1. Schematic illustration of the Cu-Cu_2O/CC preparation.

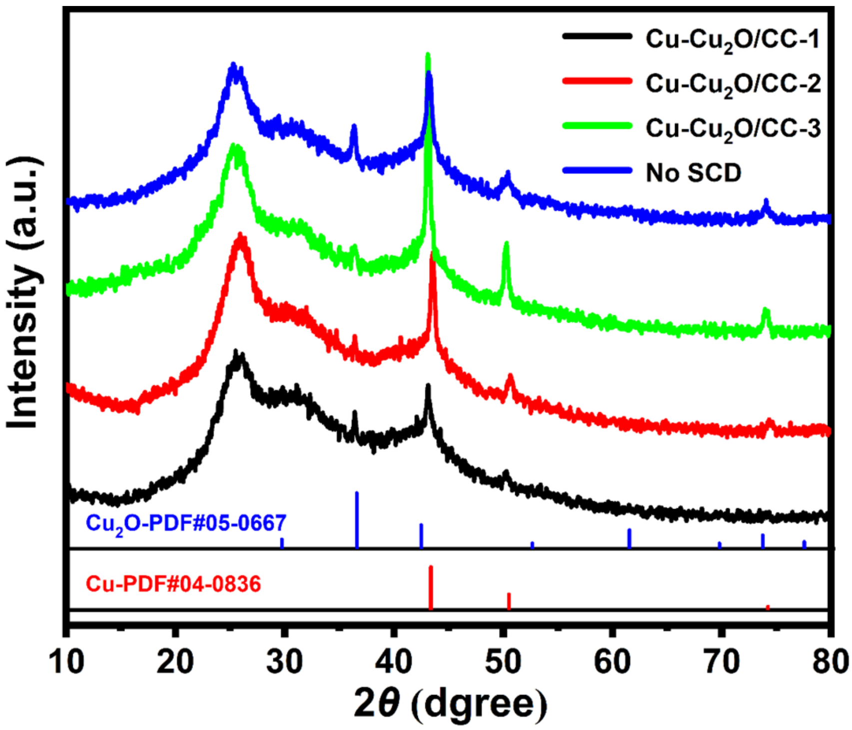

Fig. S2. XRD comparison chart of Cu-Cu_2O/CC-1, Cu-Cu_2O/CC-2, Cu-Cu_2O/CC-3 and Cu-NSCD.

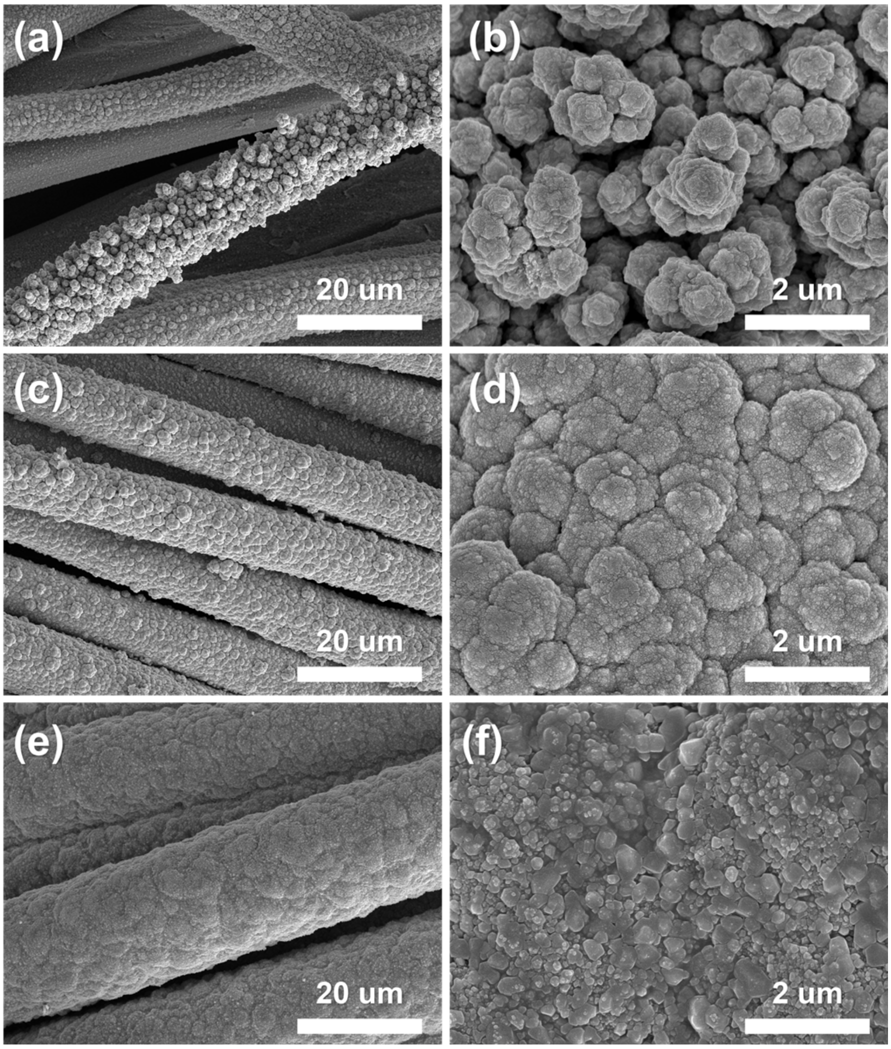

Fig. S3. SEM images of (a,b) Cu-Cu_2O/CC-1, (c,d) Cu-Cu_2O/CC-3 and (e,f) Cu-NSCD

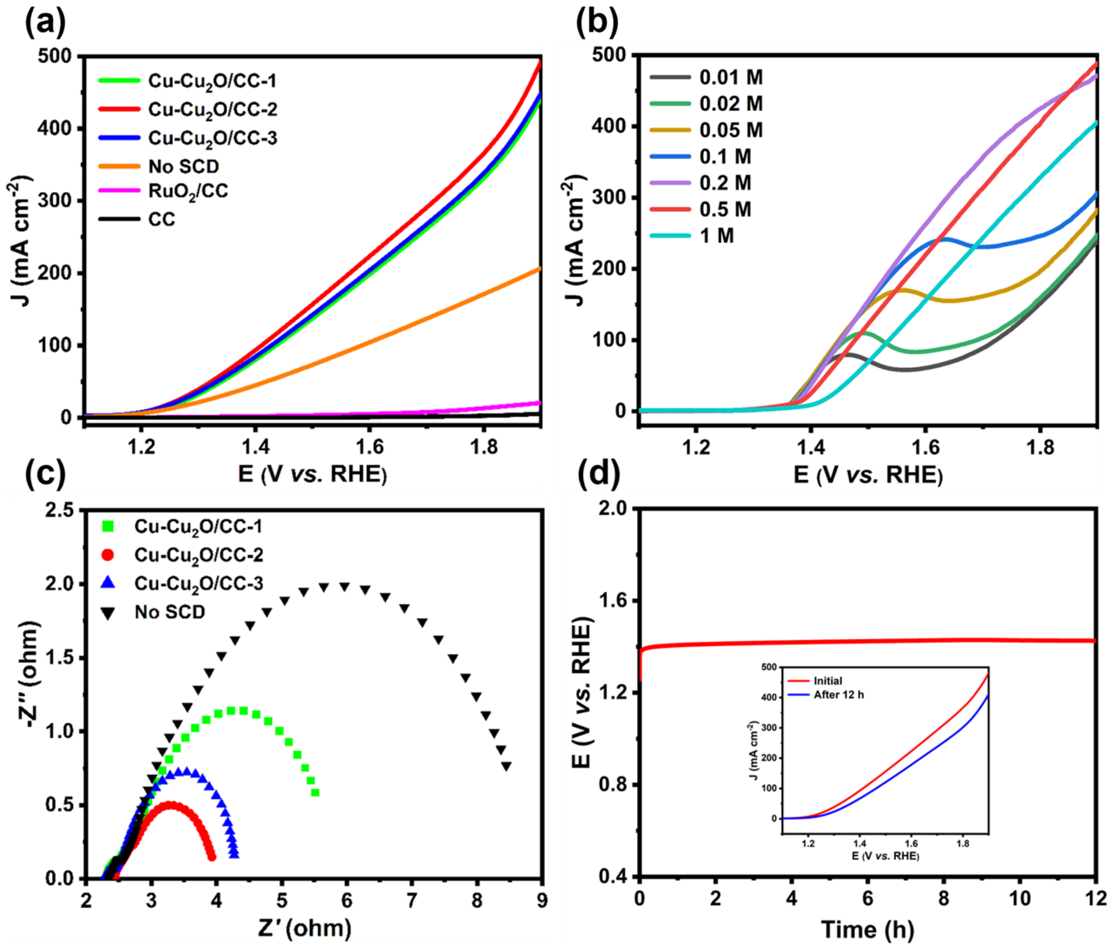

Fig. S4. (a) LSV curves of Cu-Cu_2O/CC-1, Cu-Cu_2O/CC-2, Cu-Cu_2O/CC-3, Cu-NSCD, RuO_2/CC and CC. (b) LSV curves of Cu-Cu_2O/CC-2 anode in 1.0 M KOH with and without 0.01 ~ 1 M glycerol addition. (c) Nyquist plots of Cu-Cu_2O/CC-1, Cu-Cu_2O/CC-2, Cu-Cu_2O/CC-3, Cu-NSCD for glycerol electro-oxidation process in 1.0 M KOH with 0.5 M glycerol. (d) Chronopotentiometry (CP) curve of Cu-Cu_2O/CC-2 with constant current of 10 mA cm^{-2} for 12 h and polarization curves of Cu-Cu_2O/CC before and after 12 h CP tests.

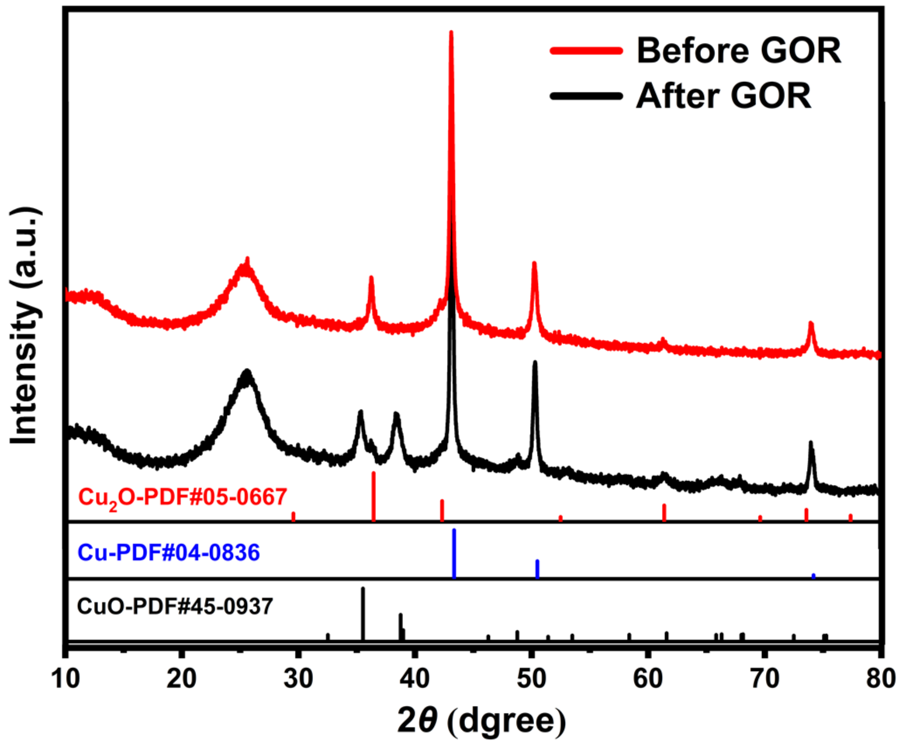

Fig. S5. XRD of Cu-Cu_2O/CC-2 before and after GOR.

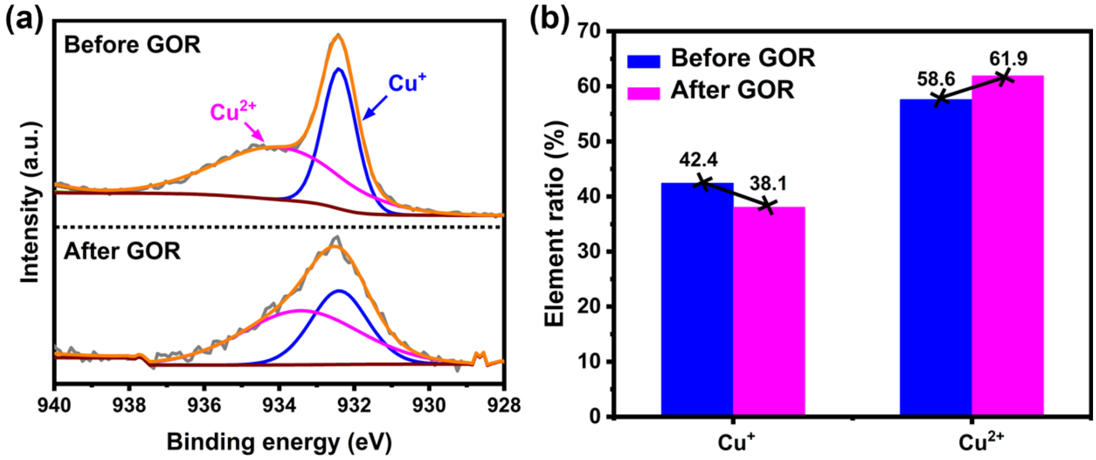

Fig. S6. Comparison chart of (a) Cu 2p high-resolution XPS spectra of Cu-Cu_2O/CC-2, (b) the elements ratio of Cu^+ and Cu^{2+} before and after GOR.

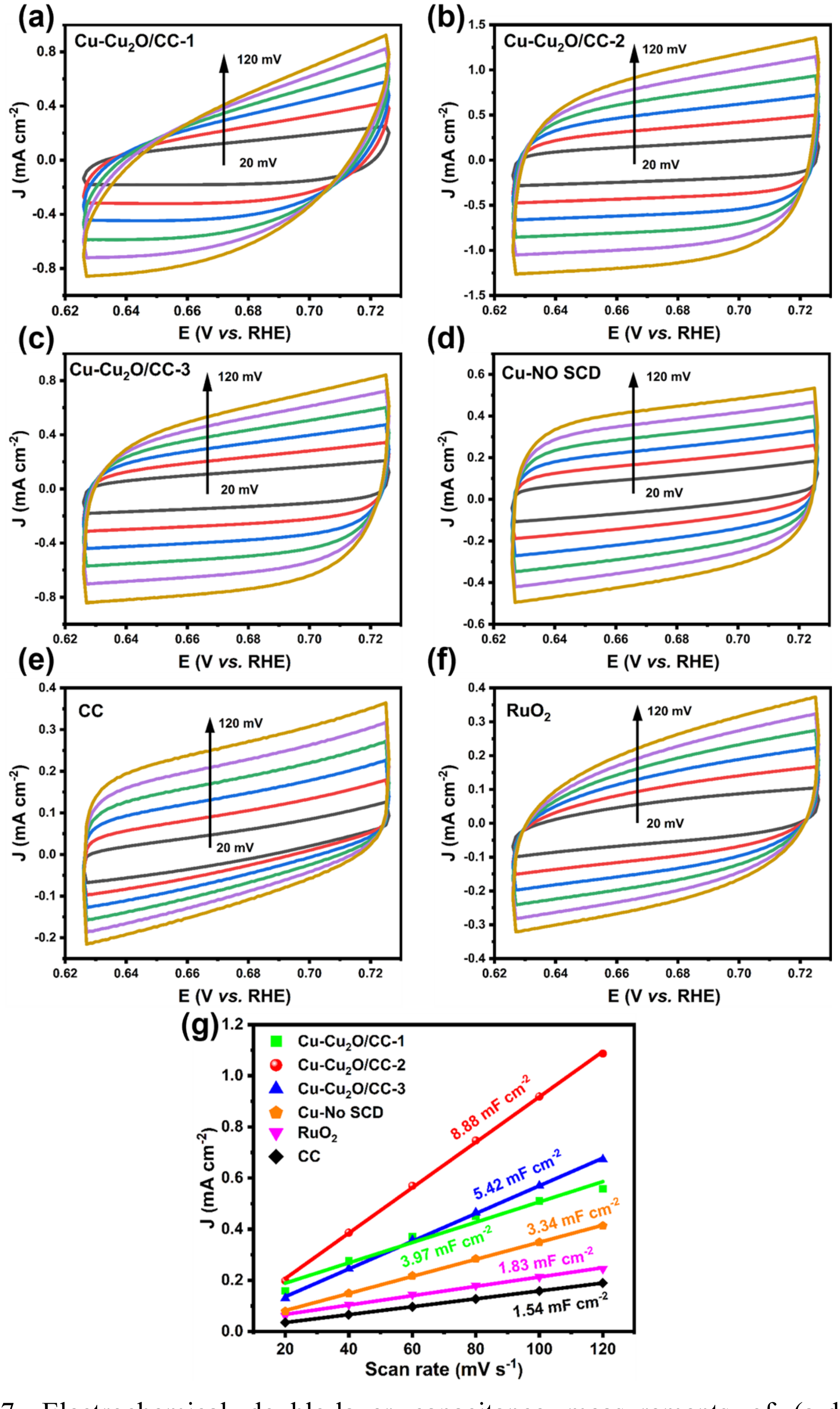

Fig. S7. Electrochemical double-layer capacitance measurements of (a-d) Cu-Cu_2O/CC-1, Cu-Cu_2O/CC-2, Cu-Cu_2O/CC-3 and Cu-NSCD. (e) CC (f) RuO_2 at scan rate of 20, 40, 60, 80, 100, and 120 mV s^{-1}. (g) Capacitive current densities as a function of scan rate at 0.67 V (vs. RHE).

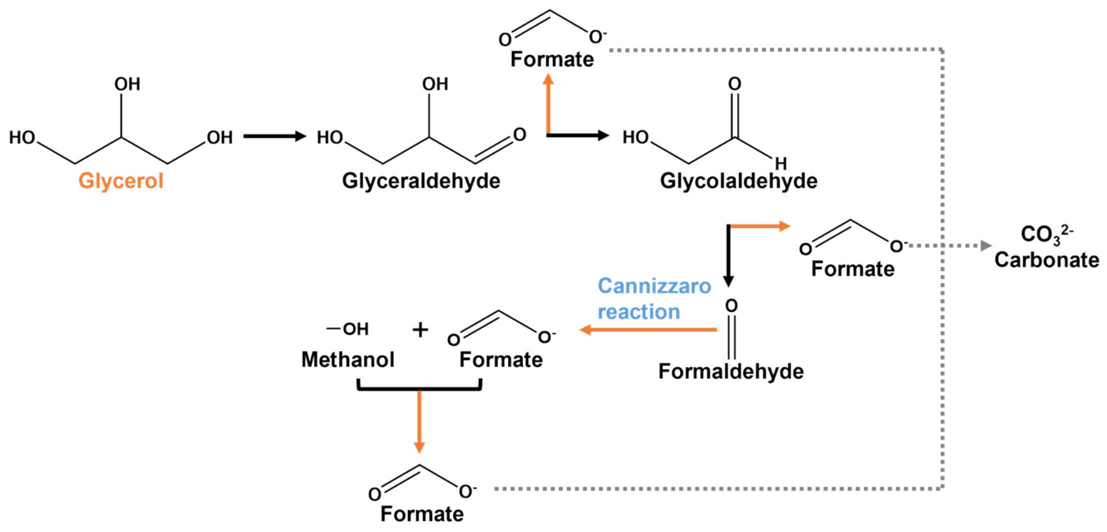

Fig. S8. Proposed mechanistic scheme of glycerol electro-catalytic oxidation to formate on Cu-Cu_2O/CC in alkaline medium.

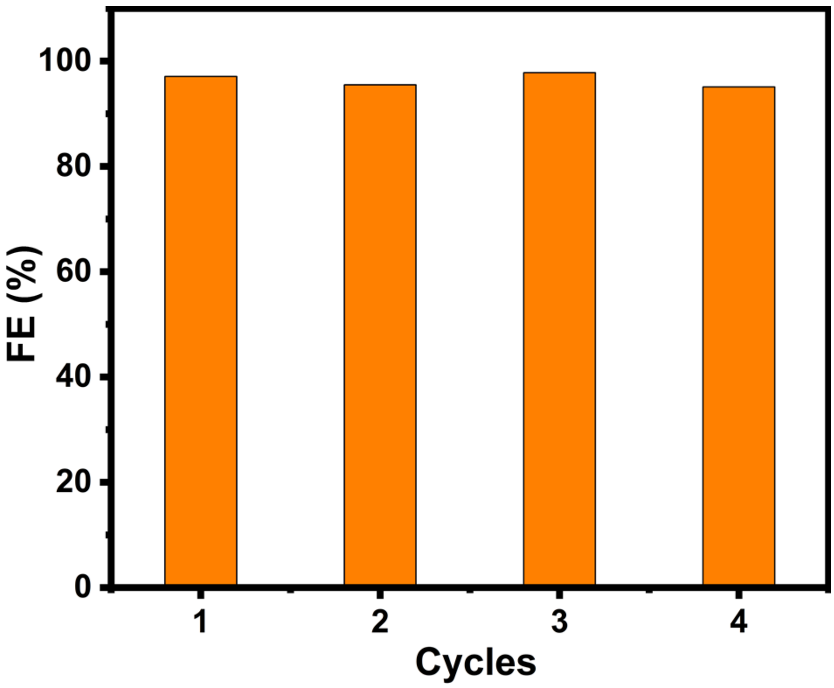

Fig. S9. The four successive cycles for corresponding Faradaic efficiencies (FEs) of formate production.

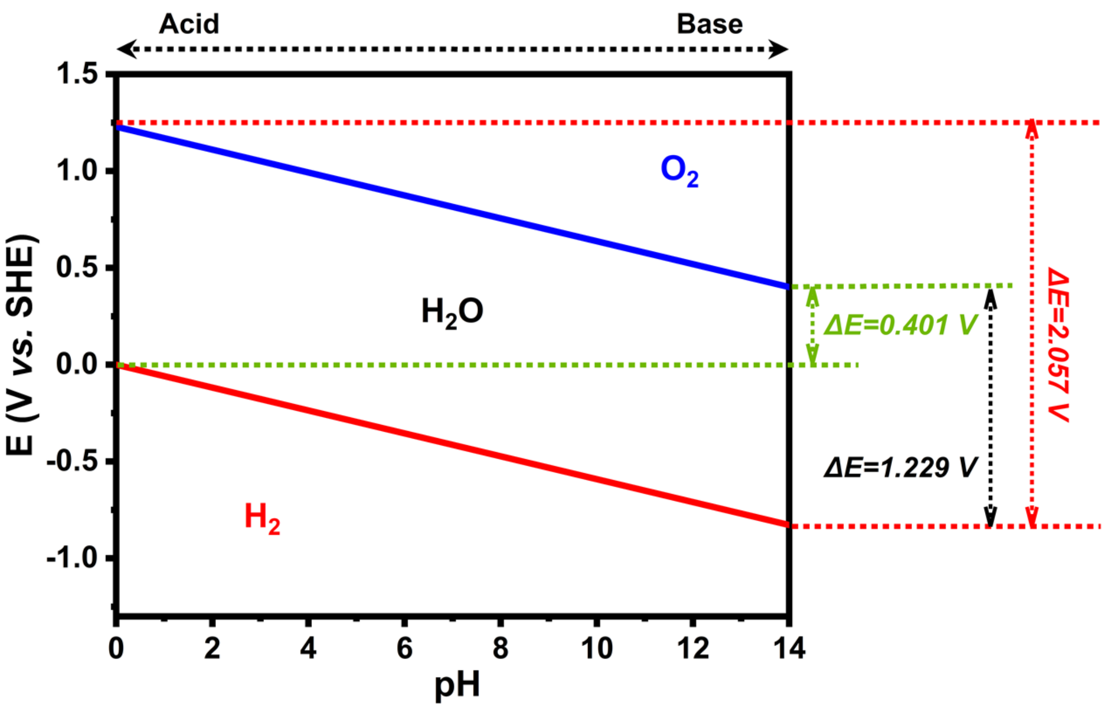

Fig. S10. The Pourbaix diagram of water that showing the theoretical potentials for the corresponding reactions.

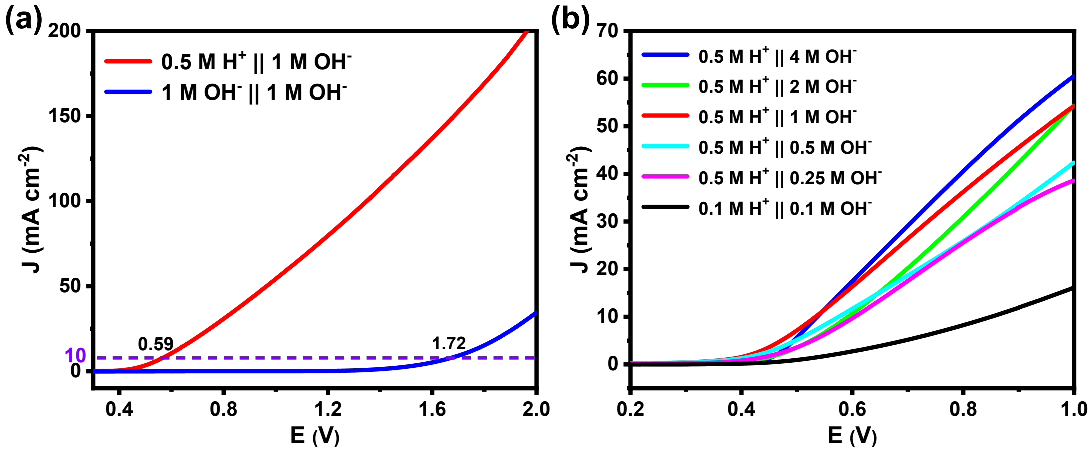

Figure S11. LSV curves of GOR (a) in hybrid acid/alkali electrolyzer and alkali/alkali electrolyzer. (b) under different pH differences.

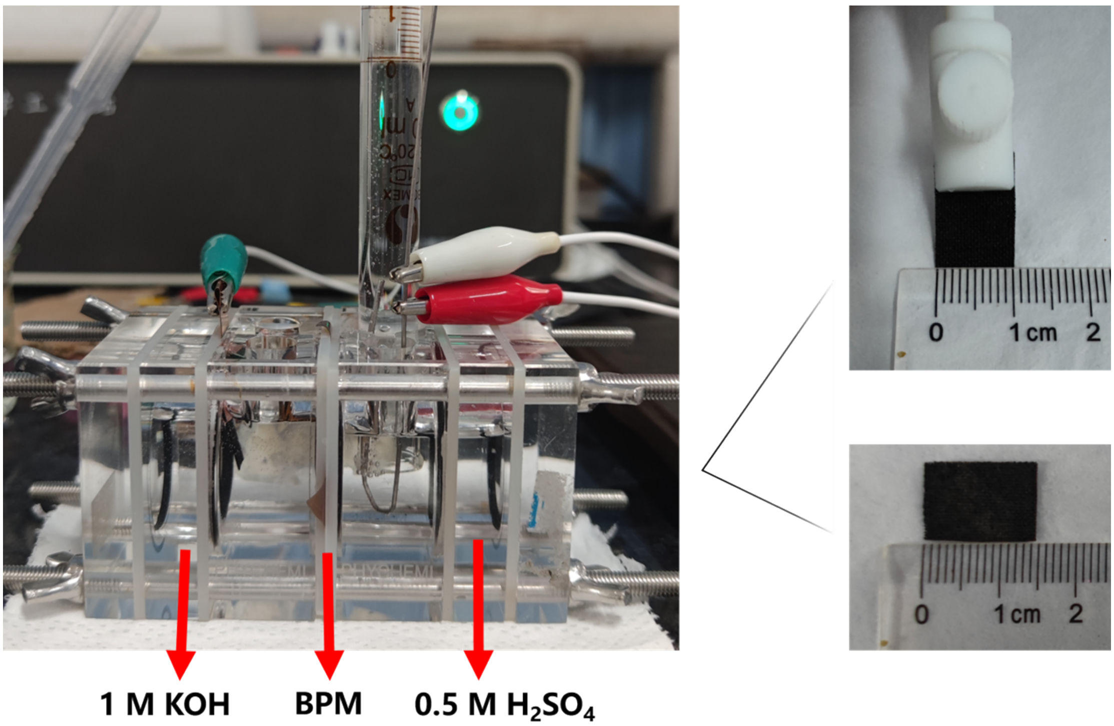

Fig. S12. Physical picture of electrolyzer and gas collection device

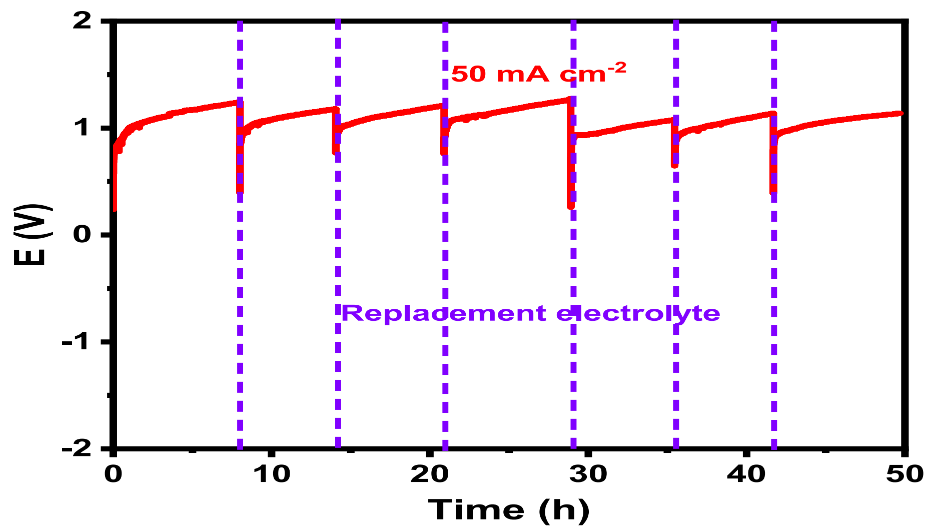

Fig. S13. Long-term stability test of Cu-Cu_2O/CC-2 at a current density of 50 mA cm^{-2}.

Table S1. Comparison of the small moleclules assisted hydrogen evolution reaction performance between the Cu-Cu_2O/CC and some other reported systems.

Catalyst	Electrolyte	Cell voltage at 10 mA cm^{-2}	Main Products	Reference
Cu-Cu_2O/CC	**1 M KOH + 0.5 M glycerol**	**0.593 V**	**Formate**	**This work**
$Co(OH)_2$@HOS/CP	1 M KOH + 3 M methanol	1.497 V	Formate	1
$Ni(OH)_2$/NF	1 M KOH + 0.5 M methanol	1.52 V	Formate	2
CoS_2 NA/Ti	1.0 M KOH + 0.3 M urea	1.59 V	N_2, CO_2	3
$Ni_{0.33}Co_{0.67}(OH)_2$/NF	1.0 M KOH+ 0.5 M methanol	1.50 V	Formate	4
Co_3S_4-NSs/Ni-F	1.0 M KOH+ 0.5 M ethanol	1.48 V	Potassium acetate	5
NiS@Ni_3S_2/$NiMoO_4$	1 M KOH + 0.5 M urea	1.40 V	N_2, CO_2	6
spherical Ni	1.0 M KOH + 0.1 M glycerol	0.58 V vs. Hg/HgO	OX, TA, GA, GLYC, LA, FA	7
$Ni_{90}Bi_{10}$	1.0 M KOH + 0.1 M glycerol	0.52 V vs. Hg/HgO	OX, TA, GA, GLYC, LA, FA	7
Ni-MoN/CFC	1.0 M KOH + 0.1 M glycerol	1.30 V vs. RHE	FA, carbonate	8

Reference:

1. K. Xiang, D. Wu, X. Deng, M. Li, S. Chen, P. Hao, X. Guo, J. L. Luo and X. Z. Fu, *Adv. Funct. Mater.*, 2020, **30**, 1909610.
2. J. Hao, J. Liu, D. Wu, M. Chen, Y. Liang, Q. Wang, L. Wang, X.-Z. Fu and J.-L. Luo, *Appl. Catal. B*, 2021, **281**, 119510.
3. S. Wei, X. Wang, J. Wang, X. Sun, L. Cui, W. Yang, Y. Zheng and J. Liu, *Electrochim. Acta*, 2017, **246**, 776-782.
4. M. Li, X. Deng, K. Xiang, Y. Liang, B. Zhao, J. Hao, J. L. Luo and X. Z. Fu, *ChemSusChem*, 2020, **13**, 914-921.
5. Y. Ding, Q. Xue, Q.-L. Hong, F.-M. Li, Y.-C. Jiang, S.-N. Li and Y. Chen, *ACS Appl. Mater. Interfaces*, 2021, **13**, 4026-4033.
6. L. Sha, T. Liu, K. Ye, K. Zhu, J. Yan, J. Yin, G. Wang and D. Cao, *Journal of Materials Chemistry A*, 2020, **8**, 18055-18063.
7. M. S. E. Houache, K. Hughes, R. Safari, G. A. Botton and E. A. Baranova, *ACS Appl. Mater. Interfaces*, 2020, **12**, 15095-15107.
8. Y. Li, X. Wei, L. Chen, J. Shi and M. He, *Nat. Commun.*, 2019, **10**, 5335.