Supporting Information

Construction of Cu³⁺-OH-Pt Interface for Enhancing Glycerol Electrooxidation Coupled with Hydrogen Evolution

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Supplementary Figures



Figure S1. SEM images of (a, c) Pt/CuO NRs and (b, d) CuO NSs.



Figure S2. The XPS survey spectra of Pt/CuO NRs and CuO NSs.



Figure S3. The XPS spectra of Cu 2p (a) and Cu LMM (b) for CuO_x.



Figure S4. The XPS spectrum of Pt 4f for Pt/CuO_x .



Figure S5. The XPS spectra of Cu 2p (a) and Cu LMM (b) for Pt/CuO_x . π ab



Figure S6. LSV curves of Pt/CuO NRs, CuO NSs in 1 M KOH with and without 50 mM glycerol addition (without *i*R-corrected).



Figure S7. Potential-Time (V-t) curve of Pt/CuO NRs under constant current (20 mA cm⁻²) in 1 M KOH for 4 hours. (The corresponding potential is 1.60 V *vs.* RHE under a constant current reaction of 20 mA cm⁻².)



Figure S8. CV curves of the (a) Pt/CuO NRs and (b) CuO NSs in non-faradic regions at different scan rates.



Figure S9. (a) ECSA, (b) area-normalized LSV, (c) mass-normalized LSV of Pt/CuO NRs and CuO NSs.



Figure S10. The calibration plots for (a) glycerol, (b) glyceric acid (c) glycolic acid, and (d) formic acid.



Figure S11. The chronoamperometric curves at different potentials (*vs.* RHE) in 1.0 M KOH with 50 mM glycerol.



Figure S12. The *FE* of FA, GLA, and GA as a function of applied potential in the reaction for 4 h over (a) Pt/CuO NRs and (b) CuO NSs.



Figure S13. (a) The S_{FA} , (b) Y_{FA} , and X during the GOR process at a constant potential of 1.40 V *vs*. RHE.



Figure S14. (a) The LSV curves of the CuO loaded with different noble metals (*i.e.*, Ru, Ag, Pd, Rh, and Pt) in 1 M KOH with and without 50mM glycerol (without *i*R-corrected). (b) The comparison of S_{FA} of the CuO loaded with different noble metals (*i.e.*, Ru, Ag, Pd, Rh, and Pt) at a constant potential of 1.40 V vs. RHE in 1.0 M KOH with 50 mM glycerol.



Figure S15. (a) The LSV curves of CuO loaded with different amounts of Pt (in μ mmol) in 1 m KOH with and without 50mM glycerol addition (without *i*R-corrected). (b) The comparison of S_{FA} for CuO loaded with different amounts of Pt at a constant potential of 1.40 V *vs*. RHE in 1.0 M KOH with 50 mM glycerol.



Figure S16. SEM images of Pt/CuO NRs (a, c) before and (b, d) after GOR in 1.0 M KOH aqueous solution at 1.4V *vs*. RHE for 4 h.



Figure S17. The XPS spectra for Cu 2p (a) and O1s (b) of Pt/CuO NRs before and after GOR in 1.0 M KOH aqueous solution at 1.4V *vs.* RHE for 4 h.



Figure S18. The XPS spectra for Pt 4f (a) and Cu LMM (b) of Pt/CuO NRs before and after GOR in 1.0 M KOH aqueous solution at 1.4V *vs.* RHE for 4 h.



Figure S19. The XPS survey spectra of Pt/CuO NRs before and after GOR in 1.0 M KOH aqueous solution at 1.4 V *vs.* RHE for 4 h.



Figure S20. Nyquist plots of (a, b) OER and (c, d) GOR at various potentials.



Figure S21. Equivalent circuits used to simulate electrochemical responses at low potential (a) and high potential (b). R_s represents the solution resistance, CPE₁ denotes the double-layer capacitance, R_{ct} is related to the interfacial charge transfer reaction, and CPE₂ and R_p are associated with dielectric properties and inner electrode resistance, respectively.

. R_p R_{ct}



Figure S22. Comparison of *X* and S_{FA} selectivity before and after drop-coating of Pt/CuO NRs with Nafion solution for 4 h at 1.40 V *vs*. RHE.



Figure S23. Theoretical mechanism understanding of glycerol electrooxidation. Reaction pathway of glycerol electrooxidation for Pt-CuOOH.

The main reaction steps were as follows. Dehydrogenation occurred at the terminal carbon atom of glycerol and the surface CuOOH, resulting in the formation of $*C_3H_7O_3$ and *O, respectively. Subsequently, *O attacked the terminal carbon atom of $*C_3H_7O_3$, forming a C-O bond and producing $*C_3H_7O_4$. This was followed by the first C-C bond cleavage of $*C_3H_7O_4$, generating the first formic acid molecule.



Figure S24. HER polarization curves of c-Pt/CuO_x electrode in 1 M KOH electrolyte.



Figure S25. (a) The comparison of the experimental and theoretical hydrogen yield. (b) The amount of generated H₂ with corresponding FEs of c-Pt/CuO_x at -1.1V *vs*. RHE.



Figure S26. The XPS spectra for (a) Pt 4f and (b) O1s of $c-Pt/CuO_x$ before and after HER in 1.0 M KOH aqueous solution at -1.1V *vs*. RHE for 1 h.



Figure S27. The XPS spectra for (a) Cu 2p and (b) Cu LMM of c-Pt/CuO_x before and after HER in 1.0M KOH aqueous solution at -1.1 V *vs*. RHE for 1 h.



Figure S28. SEM images of c-Pt/CuO_x (a, c) before and (b, d) after HER in 1.0M KOH aqueous solution at -1.1 V *vs*. RHE for 1 h



Figure S29. (a) Schematic of the production of products (end products are H_2 and KDF). (b) The model used to calculate the techno-economic analysis of the plant-gate.

Supplementary Tables

1	1			
Initial	Atomic (%)			
Pt 4f _{7/2} Pt ⁰	14.94			
Pt 4f _{7/2} Pt ²⁺	6.62			
Pt $4f_{5/2}$ Pt ⁰	27.78			
Pt 4f _{5/2} Pt ²⁺	8.77			
Cu 3p	41.89			

Table S1. Comparison of Pt 4f XPS spectral atomic percentages between pre-reactionand post-reaction samples.

After	Atomic (%)
Pt 4f _{7/2} Pt ⁰	19.60
Pt $4f_{7/2}$ Pt ²⁺	9.36
Pt 4f _{5/2} Pt ⁰	19.57
Pt $4f_{5/2}$ Pt ²⁺	7.41
Cu 3p	44.06

E	Rs	CPE ₁ -T	CPE ₁ -P	R _P	CPE ₂ -T	CPE ₂ -P	R _{CT}
1.10	2.78	0.38536	0.82095	0.117	0.22148	0.81267	36.58
1.15	2.78	0.48181	0.76031	0.046	0.30292	0.85679	21.44
1.20	2.74	0.45605	0.64692	0.035	0.49671	0.93047	6.53
1.25	2.72	0.98835	0.52131	0.027	0.55371	0.85883	3.02
1.30	2.71	1.087	0.50262	0.026	0.771	0.94488	2.06
1.35	2.69	0.46559	0.63035	0.022	0.61921	0.81121	1.99
1.40	2.70	0.39444	0.78073	0.020	0.80241	0.715	1.76
1.45	2.67	0.00162	0.77654	0.016	1.167	0.64758	2.49
1.50	2.66	0.00133	0.80474	0.013	1.417	0.65002	3.90
1.55	2.66	0.00090	0.74631	0.012	1.674	0.69402	4.95
1.60	2.67	0.00087	0.84351	0.010	1.906	0.76026	2.39

Table S2. Optimum fitting parameters of EIS data for Pt/CuO NSs under GOR conditions according to the Randles circuit model R (QR) calculated by Zsimpwin software.

Ε	Rs	CPE ₁ -T	CPE ₁ -P	R _P	CPE ₂ -T	CPE ₂ -P	R _{CT}
1.10	3.686	0.20257	0.19354	2.879	0.17423	0.93757	195.0
1.15	3.857	0.00893	0.54603	0.892	0.28465	0.90924	42.52
1.2	3.821	0.00079	0.80289	0.632	0.40691	0.87343	11.75
1.25	3.777	0.00029	0.91811	0.489	0.53191	0.82909	5.04
1.30	3.721	0.00015	0.84256	0.369	0.68426	0.77090	3.18
1.35	3.515	0.00055	0.79934	0.345	1.038	0.66206	2.26
1.40	3.477	0.00022	0.91586	0.327	1.160	0.67485	3.24
1.45	3.419	0.00016	0.97624	0.233	1.355	0.66074	4.70
1.50	3.374	0.00016	0.95432	0.174	1.423	0.68865	6.35
1.55	3.339	0.00033	0.97360	0.145	1.425	0.74729	5.86
1.60	3.323	0.00055	0.95186	0.127	1.451	0.80374	3.31

Table S3. Optimum fitting parameters of EIS data for CuO under GOR conditions

 according to the Randles circuit model R (QR) calculated by Zsimpwin software.

Reaction Type	Catalyst (Anode/Cathode)	Voltage (V) @ Current Density	Electrolyte	Stability (h)	Ref.
Flow cell	NC/Ni-Mo-N/NF	1.38 V @ 10 mA/cm ²	1 M KOH+ 0.1 M Glycerol	12	1
MEA	Mn-Co-S/NF Pt/C/NF	1.38 V @ 100 mA/cm ²	1 M KOH+ 0.3 M Glycerol	12	2
Flow cell	S-CuO/CF (GOR) Pt/C (HER)	1.2 V @ 10 mA/cm ²	1 М КОН	10	3
Flow cell	CoNi film	1.46 V @ 10 mA/cm ²	1 M KOH + 0.33 M Glycerol	20	4
Flow cell	Ni ₃ N/Co ₃ N-NWs	1.79 V @ 400 mA/cm ²	1 M NaOH + 0.1 M Glycerol	200	5
Flow cell	NiCo ₂ O ₄ /NF (GOR) Ni form (HER)	1.35 V @ 10 mA/cm ²	1 M NaOH + 0.1 M Glycerol	-	6
Flow cell	Ru-CoP ₂	1.41 V @ 100 mA/cm ²	1 M KOH + 0.1 M Glycerol	50	7
MEA	Pt/CuO NRs (GOR) \parallel c- Pt/CuO _x (HER)	1.55 V @ 100 mA/cm ²	1 M KOH + 0.05 M Glycerol	~100	This work

 Table S4. Comparison of Glycerol Coupling Hydrogenation (GOR-HER)

Performance.

Supplementary Notes

Notes S1. The production of potassium dicarboxylate from formate is a viable route, with potassium dicarboxylate(KDF) being more competitive. In order to investigate the economic feasibility of this process for KDF upgrading and recycling, a simplified techno-economic analysis was carried out using an adapted model and the separation process is shown in Figure S24.⁸

The calculated assumed costs are as follows.

1. The cost of the electrolyzer is assumed to be 460 m⁻²,⁹ the cost of the separation material is 5% of the cost of the electrolyzer, and the cost of the catalyst and membrane is 5% of the cost of the electrolyzer.

2. A capacity factor of 0.95 is assumed for one day of plant operation, and the plant will operate for 22.8 hours per day.¹⁰

3. The electrocatalytic production of formate to KDF is assumed to have a yield of 70% and a Faraday efficiency of 100% for hydrogen.¹¹

4. The plant lifetime is assumed to be 30 years.¹²

5. The cost of electricity is assumed to be 1 to 20 $\text{e/kWh}^{-1.13}$ The cost of electricity includes two components, the electrolyzer for FA and H₂ electrolysis, and the product separation equipment. The cost of electricity for product separation is assumed to be equal to the cost of electrolysis.

6. The input chemicals include water, formic acid, potassium hydroxide, and glycerol, and the output chemicals include KDF and H₂.

7. Both operation and maintenance costs are assumed to be 5% of the capital cost.¹³

Cost Calculation

1. Capital cost

Capital cost = (Electrolyzer cost + Catalyst and membrane cost + Speparation material cost) / Plant lifetime (day)

• Electrolyzer cost = Area of electrolyser \times 460 \$ m⁻²

Area of electrolyser (m-2) = I / i

(Where I is the required current and i is the current density)

- Catalyst and membrane $cost = Electrolyzer cost \times 5\%$
- Speparation material $cost = Electrolyzer cost \times 5\%$

2. Maintenance costs

Maintenance costs = Capital cost \times 5%

3. Balance of plant

Balance of plant = Capital cost × Balance of plant factor

(Where balance of plant factor is 0.2)

4. Installation cost

Installation $cost = Capital cost \times Lang factor$

(Where Lang factor is 0.35)

5. Operation costs

Operation costs = Capital cost \times 5%

6. Electricity cost

Electricity costs per day = Electrolyser electricity cost of per day + Speparation material electricity costs of per day

Electrolyser electricity cost of per day = Energy use per day × Cost per kWh Energy use per day = P × Capacity factor ×Time in a day (h)

- \blacktriangleright P = U × I/1000
- \blacktriangleright I = Q / (Time in a day(s) × Capacity factor)

ightarrow Q = (Mass of glycerol × F × N) / (Molar mass of glycerol × Faradaic efficiency)(Where "P" is the power. U is the operational cell potentials. The conversion ofglycerol to formic acid transfers 8/3 electrons and N takes the value of 8/3. F is theFaraday's constant. Q is the charge required to process one ton of glycerol. Faradayefficiency takes the value of formate.) Speparation material electricity costs of per day = Electrolyser electricity cost of per day

7. Input chemicals costs

Input chemicals costs = Cost of glycerol \times Mass of glycerol needed + Cost of KOH \times Mass of KOH needed + Cost of formic acid \times Mass of formic acid needed + Cost of water \times Mass of water needed

Chemicals require 1 ton of glycerol, 2.44 ton of KOH, 2.5 ton of FA and 108.60 tons of water.¹¹

Product	Price (\$ / ton)			
Feedstocks				
glycerol	110 ¹⁴			
FA	40015			
КОН	1280 ¹⁶			
Water	0.2216			
Products				
KDF	1590ª			
H ₂	190017			

ahttps://jiage.molbase.cn/hangqing/

Product value

Product value = Cost of KDF \times Mass of KDF obtained + Cost of H₂ \times Mass of H₂

obtained

• Per ton of glycerol can yield 3.96 ton of KDF.

• Mass of H_2 obtained = Q × Molar mass of $H_2 / (n \times F)$

(Where n is 2)

Based on the LSV curve measured from the MEA, we selected two different current densities, 100 and 300 mA cm⁻², along with their corresponding potentials 1.55 and 2.10 V, to calculate the plant-gate levelized costs. When calculating the current prices, we assumed that FEFA is 80% and the electricity price is \$ 0.02/kWh.

Supplementary reference

- Y. Xu, M. Liu, S. Wang, K. Ren, M. Wang, Z. Wang, X. Li, L. Wang, H. Wang, *Appl. Catal. B Environ.* 2021, 298, 120493.
- Y. Fang, C. Dai, X. Liu, Y. Wang, C. Ju, S. He, R. Shi, Y. Liu, J. Zhang, Y. Zhu, J. Wang, *Nano Energy* 2024, 127, 109754.
- R.-Y. Fan, X.-J. Zhai, W.-Z. Qiao, Y.-S. Zhang, N. Yu, N. Xu, Q.-X. Lv, Y.-M. Chai, B. Dong, *Nano-Micro Lett.* 2023, 15, 190.
- M. R. Rizk, M. G. Abd El-Moghny, H. H. Abdelhady, W. M. Ragheb, A. H. Mohamed, H. F. Fouad, M. Mohsen, A. S. Kamel, M. S. El-Deab, *Int. J. Hydrogen Energy* 2022, 47, 32145.
- Y. Zhu, Q. Qian, Y. Chen, X. He, X. Shi, W. Wang, Z. Li, Y. Feng, G. Zhang, F. Cheng, *Adv. Funct. Mater.* 2023, 33, 2300547.
- G. Wu, X. Dong, J. Mao, G. Li, C. Zhu, S. Li, A. Chen, G. Feng, Y. Song, W. Chen, W. Wei, *Chem. Eng. J.* 2023, 468, 143640.
- B. Deng, J. Shen, J. Lu, C. Huang, Z. Chen, F. Peng, Y. Liu, *J. Energy Chem.* 2025, 100, 317.
- H. Zhou, Y. Ren, Z. Li, M. Xu, Y. Wang, R. Ge, X. Kong, L. Zheng, H. Duan, *Nat. Commun.* 2021, 12, 4679.
- 9. B. You, N. Jiang, X. Liu, Y. Sun, Angew. Chem. Int. Ed. 2016, 55, 9913.
- Patel, D. Schwartz, X. Wang, R. Lin, O. Ajao, A. Seifitokaldani, ACS Sustainable Chem. Eng. 2022, 10, 4206-4217.
- Y. Wang, Y.-Q. Zhu, Z. Xie, S.-M. Xu, M. Xu, Z. Li, L. Ma, R. Ge, H. Zhou, Z. Li, X. Kong, L. Zheng, J. Zhou, H. Duan, ACS Catl. 2022, 12, 12432-12443.

- L. Jiang, A. Gonzalez-Diaz, J. Ling-Chin, A. Malik, A. P. Roskilly, A. J. Smallbone, *Nat. Sustain.* 2020, 3, 761-767.
- P. De Luna, C. Hahn, D. Higgins, S. A. Jaffer, T. F. Jaramillo, E. H. Sargent, Science 2019, 364, eaav3506.
- 14. G. Dodekatos, S. Schünemann, H. Tüysüz, ACS Catl. 2018, 8, 6301-6333.
- 15. J. Eppinger, K.-W. Huang, ACS Energy Lett. 2017, 2, 188-195.
- 16. W.-J. Liu, Z. Xu, D. Zhao, X.-Q. Pan, H.-C. Li, X. Hu, Z.-Y. Fan, W.-K. Wang, G.-H. Zhao, S. Jin, G. W. Huber, H.-Q. Yu, *Nat. Commun.* 2020, 11, 265.
- W. R. Leow, Y. Lum, A. Ozden, Y. Wang, D.-H. Nam, B. Chen, J. Wicks, T.-T. Zhuang, F. Li, D. Sinton, E. H. Sargent, *Science* 2020, 368, 1228.