

Supporting Information

Synthesis of IrCu/Co₃O₄ hybrid nanostructures and their enhanced catalytic properties toward oxygen evolution reaction under both acidic and alkaline conditions

Xiaomei Xu¹, Taekyung Yu^{1,*}

¹ Department of Chemical Engineering, Integrated Engineering Major, College of Engineering, Kyung Hee University, Yongin, 17104, Republic of Korea

*Corresponding author

E-mail addresses: tkyu@khu.ac.kr (T. Yu)

1. Electrochemical Characterization.

All electrochemical measurements were carried out at ambient temperature and pressure with an electrochemical workstation (CHI760E, Chenhua Shanghai). A three-electrode cell configuration was employed with a working electrode of glassy carbon with a working area of 0.07 cm², a counter electrode of graphite rod. The Hg/HgO (Re-61AP, ALS), and Ag/AgCl were the reference electrodes under the alkaline and acidic conditions, respectively. Electrocatalyst inks were prepared by dispersing 2 mg of catalyst into a solution containing 45 µL of 5% Nafion solution (Du Pont) and 555 µL of ultrapure water-ethanol solution with equal volumes of water and ethanol, followed by ultrasonication for 0.5 h. Before each experiment, the glassy carbon electrode was polished with 0.05 µm alumina for 0.2 h until it achieved a mirror shine. Then, 3.4 µL of the catalyst solution was transferred onto a glassy carbon electrode and fully dried at 25 °C.

The overpotential (η) was calculated by $\eta = E(\text{vs. RHE}) - 1.23 \text{ V}$ for OER. In addition, the 90% iR correction was done for the polarization curves. Electrochemical impedance spectroscopy (EIS) analysis was conducted at 1.50-1.65 V vs. RHE in the frequency range from 100 k to 0.01 Hz and the EIS plots were fitted using ZView software. To compare the electrochemically active surface area (ECSA) of each catalyst, the double-layer capacitance (C_{dl}) was measured in 1.0 M KOH (0.5 M H₂SO₄) in the non-Faradaic region at the scan rates of 20, 40, 60, 80, and 100 mV·s⁻¹.

$$C_{dl} = (\Delta j = (j_a - j_c))/2 \quad (1)$$

Turnover Frequency (TOF) is a measure of catalytic activity. It refers to the number of times a catalytic site converts a substrate into a product per unit time. It's a critical parameter for evaluating the efficiency of catalysts in chemical reactions¹.

$$\text{TOF} = I/4nF \quad (2)$$

where I is the current density at a definite overpotential; F is the Faraday's constant (96,485 C·mol⁻¹); and n, the number of moles of the electrochemical materials on the electrode. The factors 4 are based on the assumption that four electrons are necessary to form one oxygen molecule².

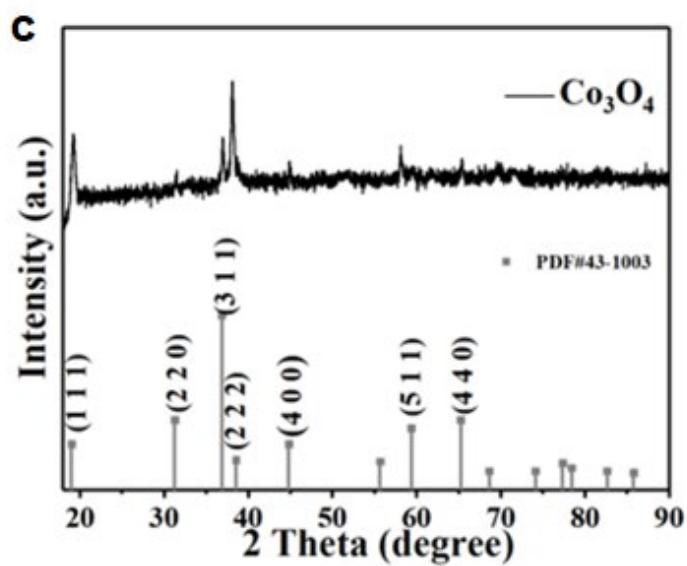
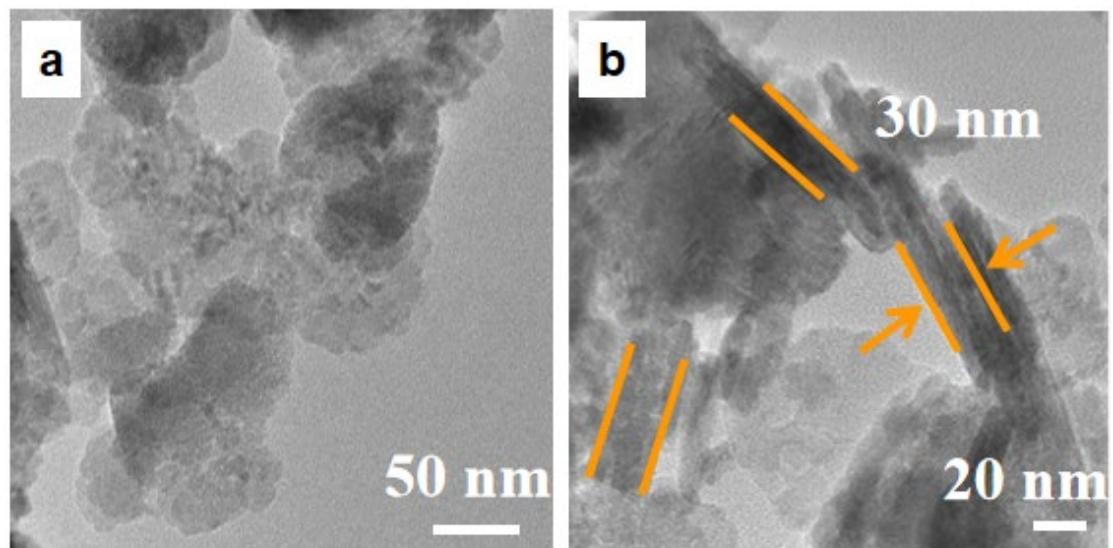


Fig. S1. (a and b) TEM images and (c) XRD patterns of Co₃O₄ nanosheets.

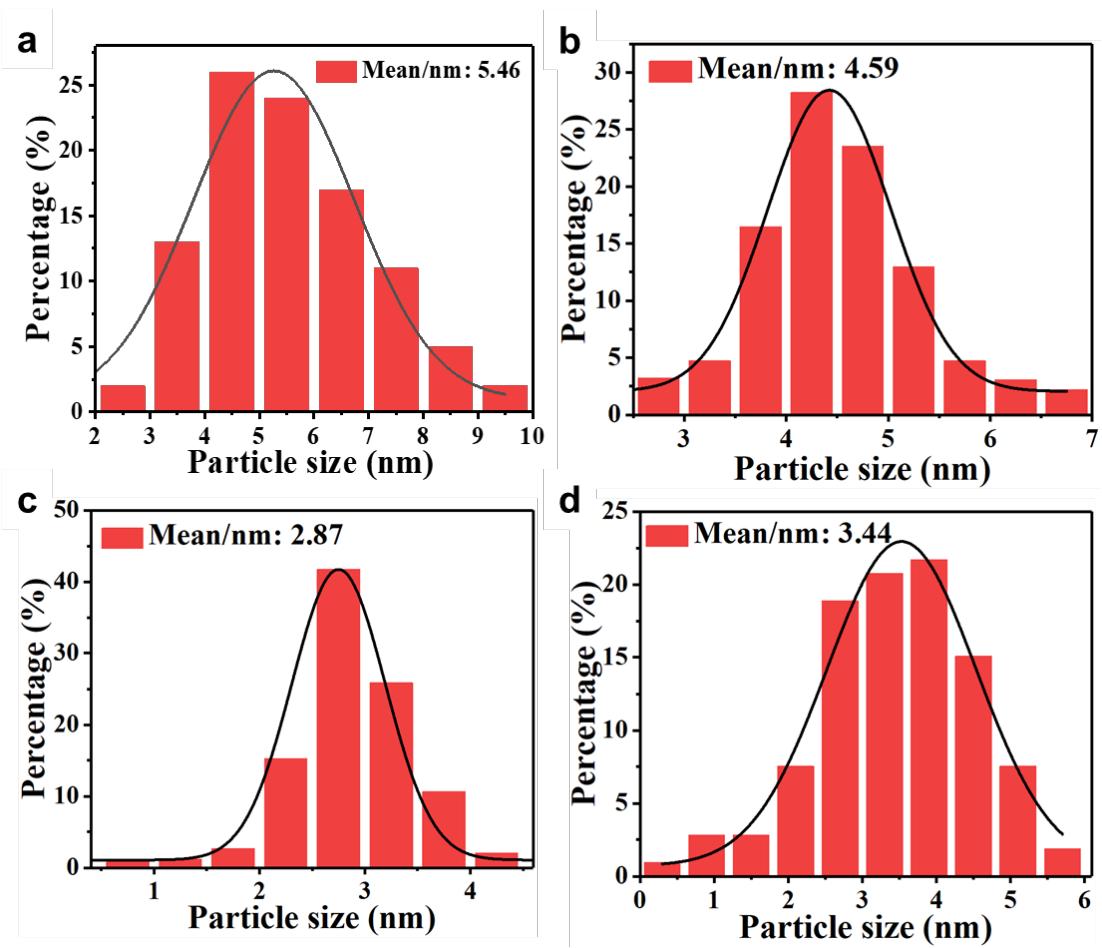


Fig. S2. Size distribution diagrams of the (a) Ir₂₆Cu₇₄ nanoparticles (b) Ir₁₉Cu₈₁/Co₃O₄, (c) Ir₂₆Cu₇₄/Co₃O₄, and (d) Ir₃₂Cu₆₈/Co₃O₄, respectively.

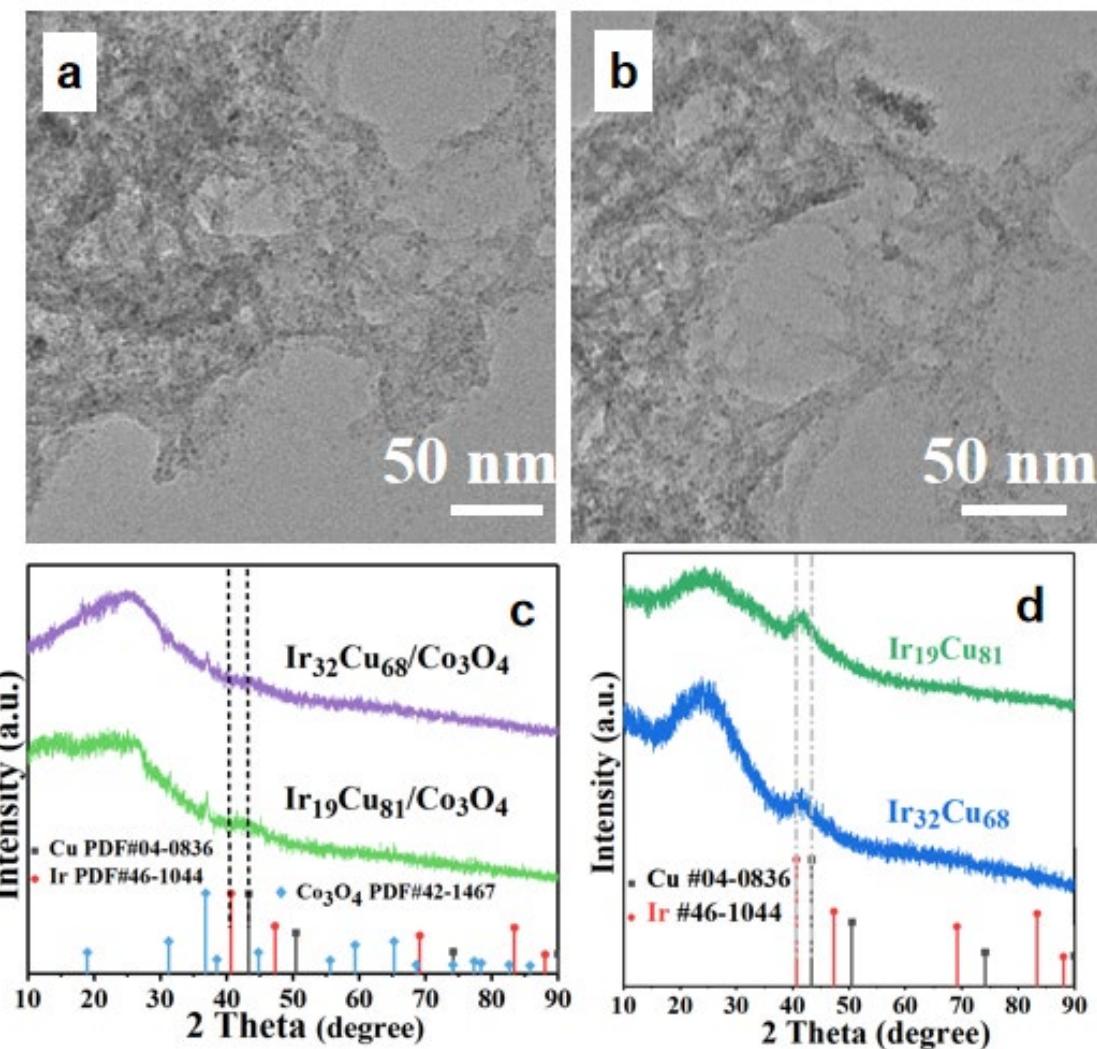


Fig. S3. TEM images of the (a) $\text{Ir}_{19}\text{Cu}_{81}/\text{Co}_3\text{O}_4$ and (b) $\text{Ir}_{32}\text{Cu}_{68}/\text{Co}_3\text{O}_4$. (c) XRD patterns of the $\text{Ir}_{19}\text{Cu}_{81}/\text{Co}_3\text{O}_4$ and $\text{Ir}_{32}\text{Cu}_{68}/\text{Co}_3\text{O}_4$. (d) XRD patterns of the $\text{Ir}_{19}\text{Cu}_{81}$ and $\text{Ir}_{32}\text{Cu}_{68}$.

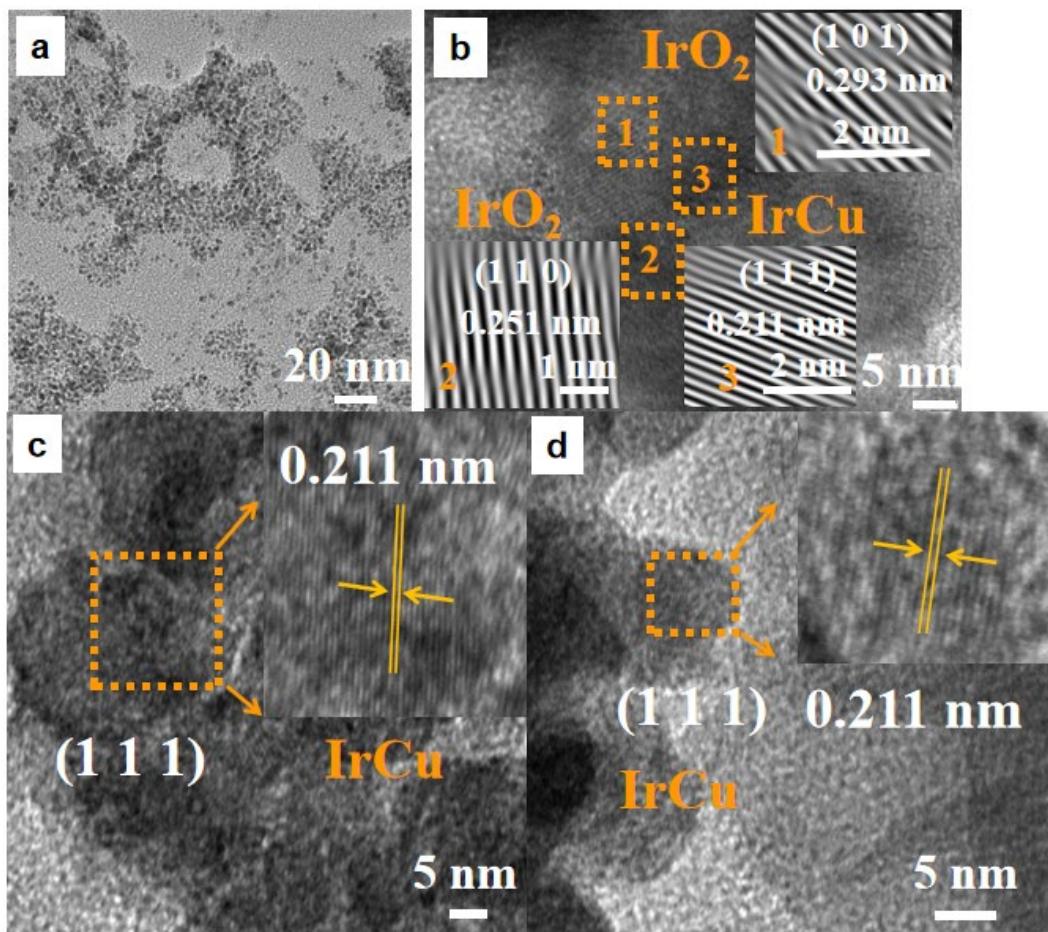


Fig. S4. (a) TEM and (b, c, d) HRTEM images of the Ir₂₆Cu₇₄ nanoparticles

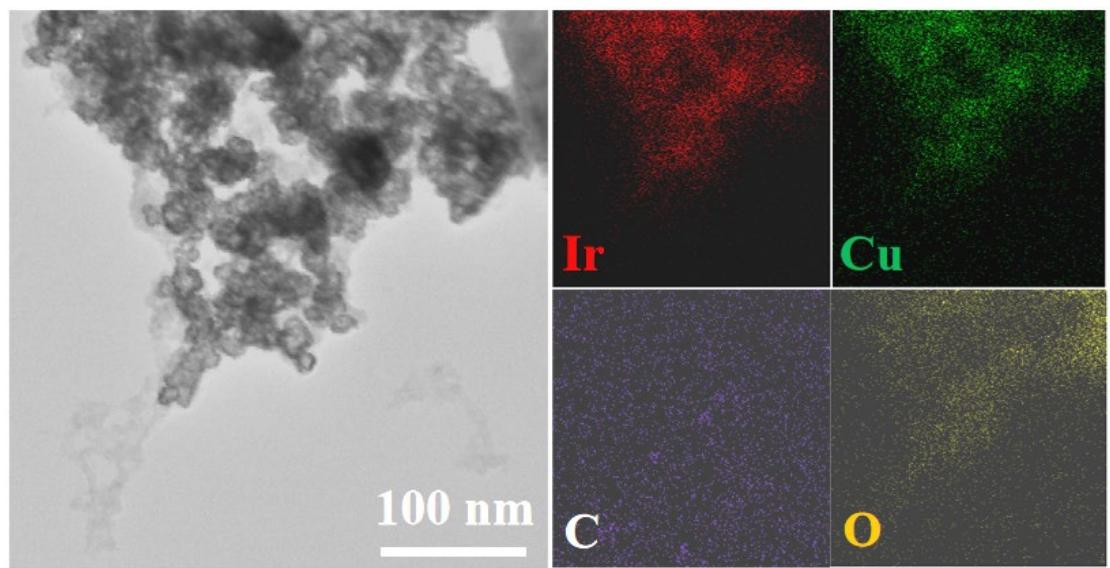


Fig. S5. TEM EDS Mapping images of the Ir₂₆Cu₇₄ NPs.

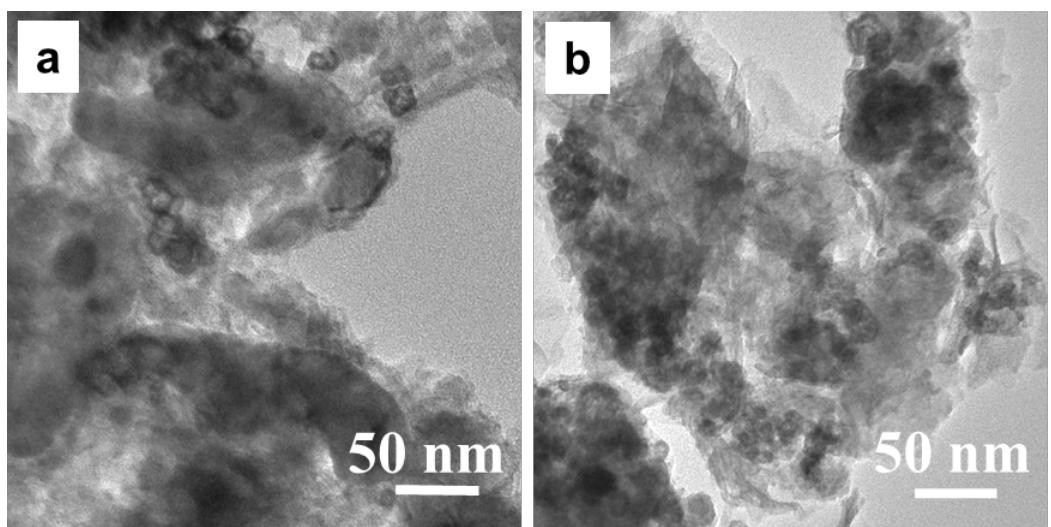


Fig. S6. TEM images of the $\text{Ir}_{26}\text{Cu}_{74}/\text{Co}_3\text{O}_4$ after OER stability test in (a) 1.0 M KOH and (b) 0.5 M H_2SO_4 solutions, respectively.

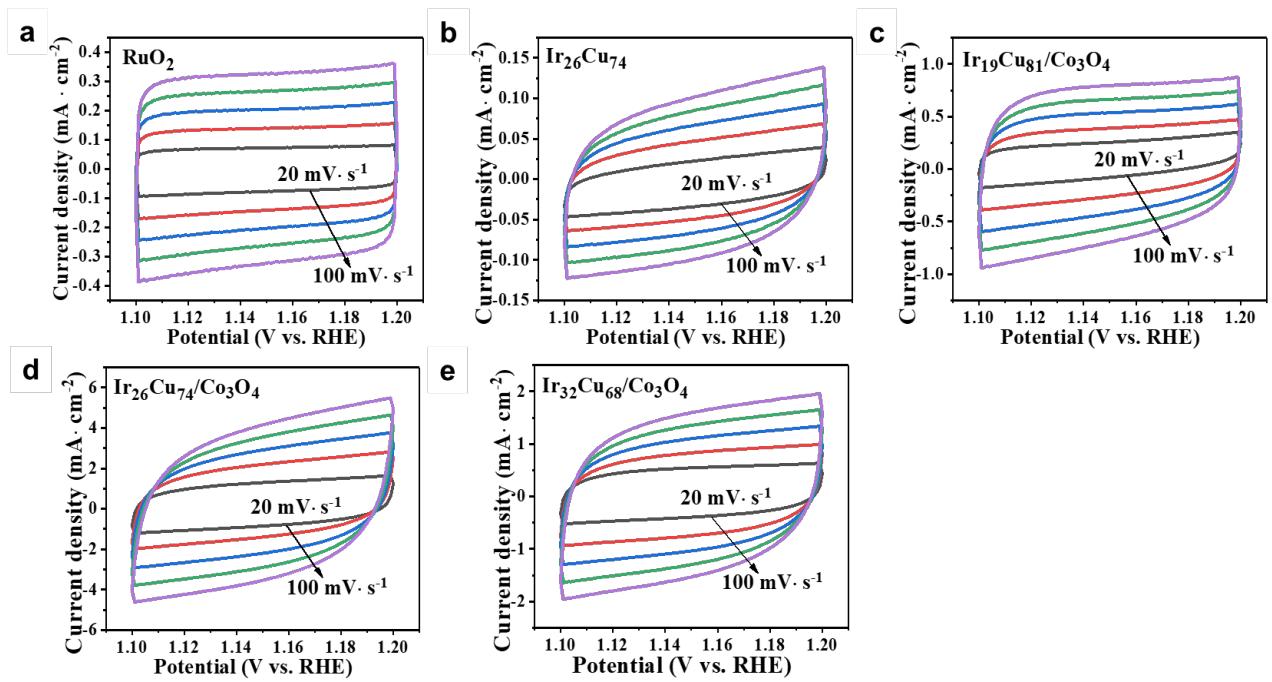


Fig. S7 CV curves of the (a) commercial RuO₂, (b) Ir₂₆Cu₇₄, (c) Ir₁₉Cu₈₁/Co₃O₄, (d) Ir₂₆Cu₇₄/Co₃O₄, and (e) Ir₃₂Cu₆₈/Co₃O₄ at different scan rates in a 1.0 M KOH solution.

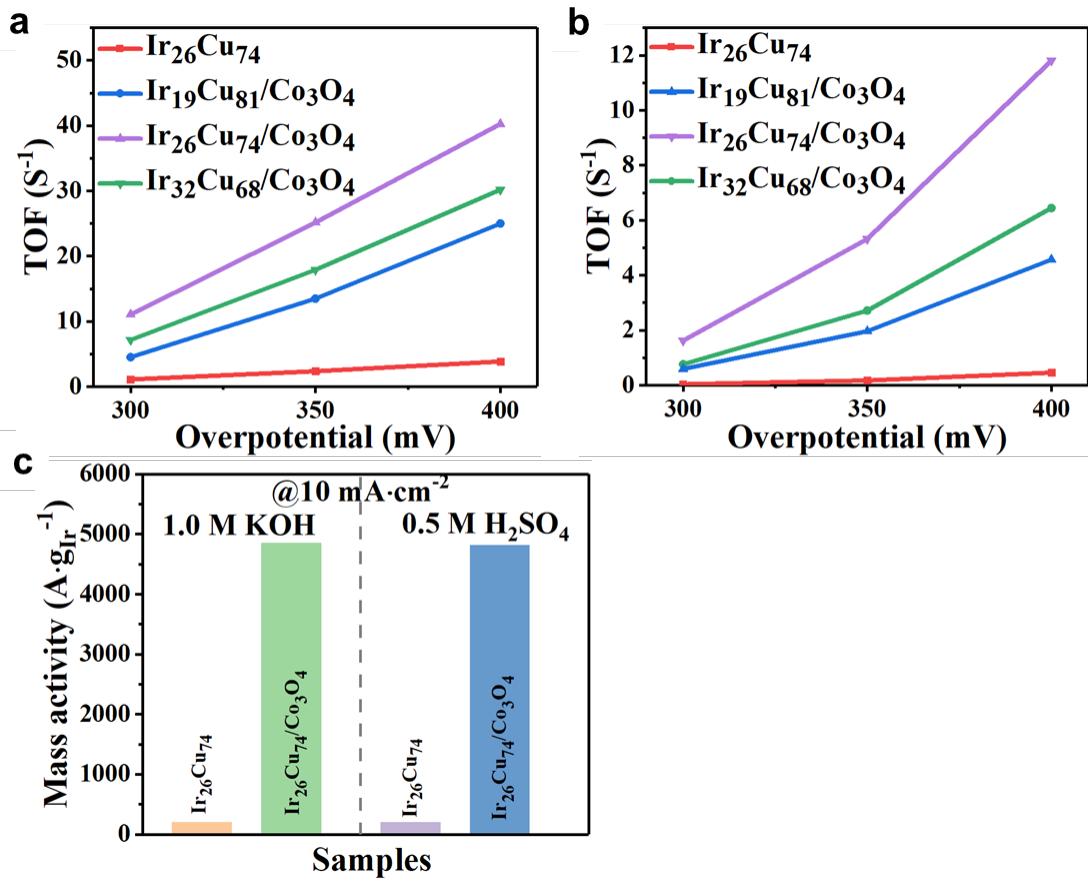


Fig. S8. TOFs of the $\text{Ir}_{26}\text{Cu}_{74}$, $\text{Ir}_{19}\text{Cu}_{81}/\text{Co}_3\text{O}_4$, $\text{Ir}_{26}\text{Cu}_{74}/\text{Co}_3\text{O}_4$, and $\text{Ir}_{32}\text{Cu}_{68}/\text{Co}_3\text{O}_4$ calculated in an (a) alkaline and (b) acidic conditions, respectively. (c) Mass activity of the $\text{Ir}_{26}\text{Cu}_{74}$ and $\text{Ir}_{26}\text{Cu}_{74}/\text{Co}_3\text{O}_4$.

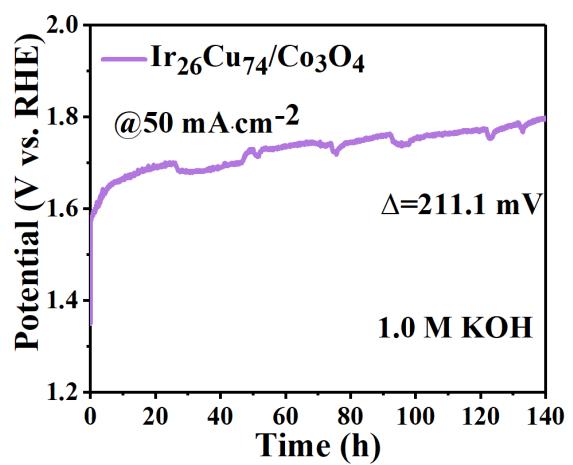


Fig. S9. Durability of the Ir₂₆Cu₇₄/Co₃O₄ in a 1.0 M KOH solution.

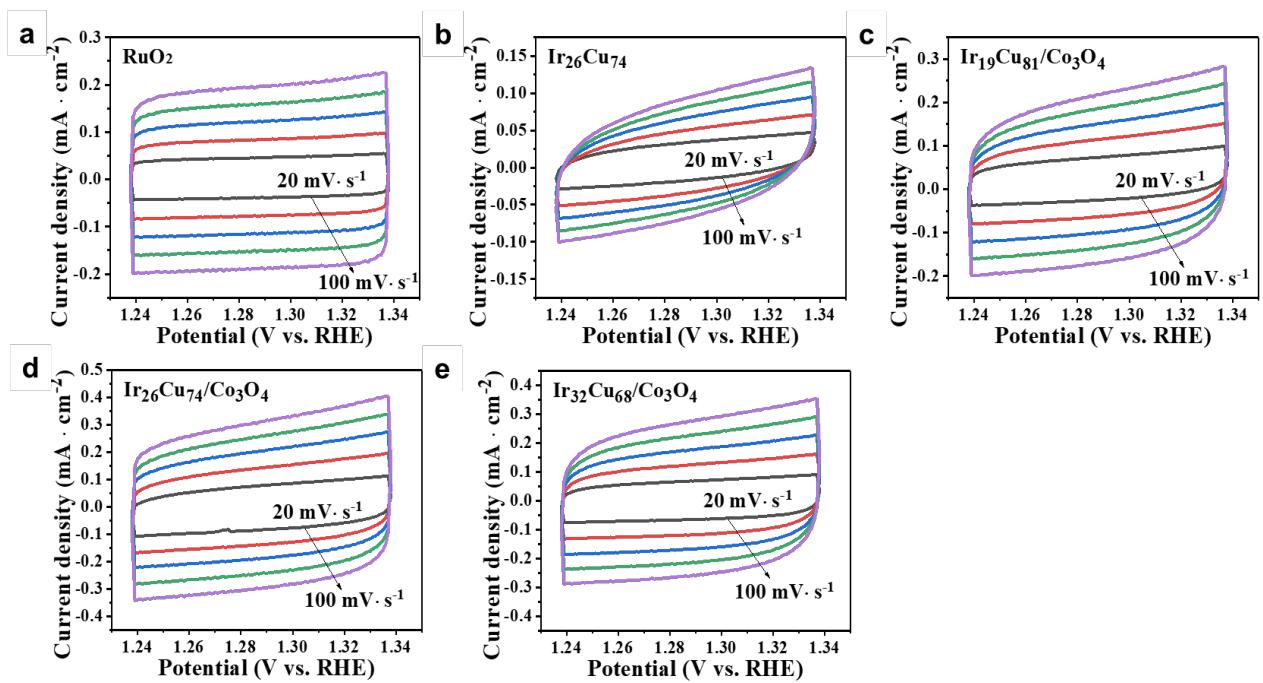


Fig. S10. CV curves of the (a) commercial RuO₂, (b) Ir₂₆Cu₇₄, (c) Ir₁₉Cu₈₁/Co₃O₄, (d) Ir₂₆Cu₇₄/Co₃O₄, and (e) Ir₃₂Cu₆₈/Co₃O₄ at different scan rates in a $0.5 \text{ M H}_2\text{SO}_4$ solution.

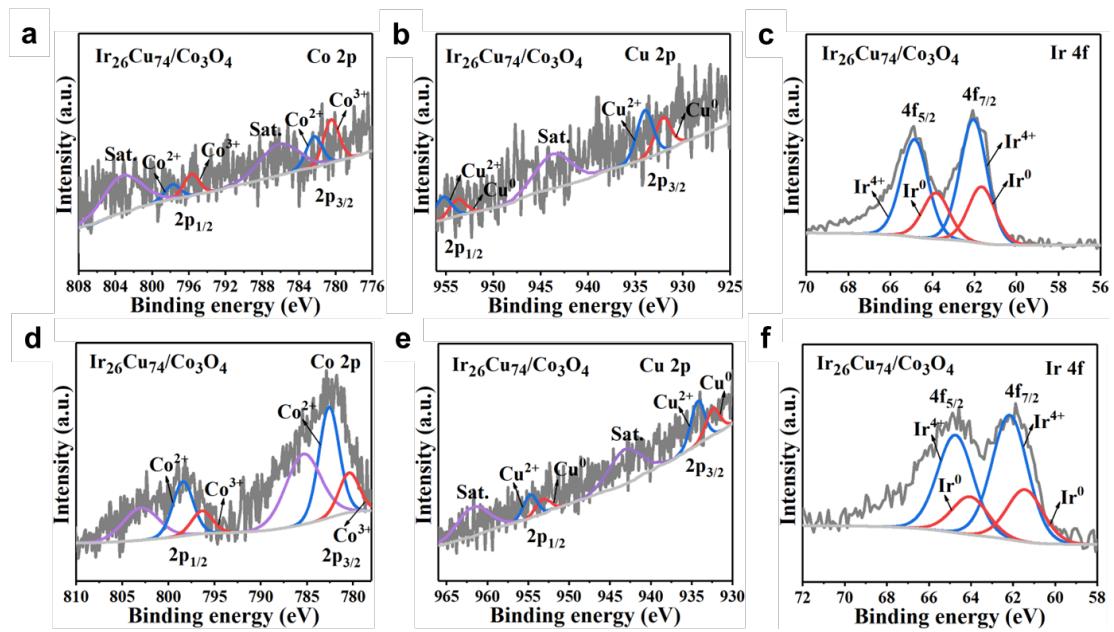


Fig. S11. XPS spectra of the $\text{Ir}_{26}\text{Cu}_{74}/\text{Co}_3\text{O}_4$ after OER stability test in (a to c) alkaline and (d to f) acidic conditions, respectively.

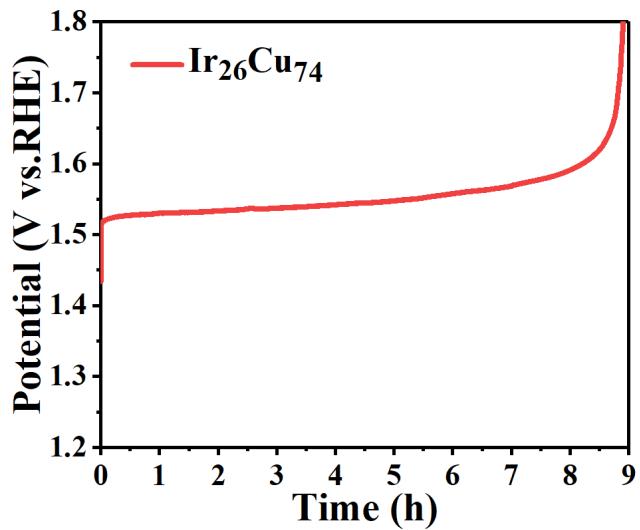


Fig. S12. OER stability test result of the $\text{Ir}_{26}\text{Cu}_{74}$ in a 1.0 M KOH solution

Table S1. ICP data of the IrCu/Co₃O₄.

Samples	C _{Ir} (mg/mL)	C _{Cu} (mg/mL)	Ir, Cu Mole ration
Ir ₁₉ Cu ₈₁ /Co ₃ O ₄	0.87	1.23	0.23:1
Ir ₂₆ Cu ₇₄ /Co ₃ O ₄	1.24	1.16	0.36:1
Ir ₃₂ Cu ₆₈ /Co ₃ O ₄	1.50	1.13	0.47:1

Table S2. XPS data of the Ir₂₆Cu₇₄, Ir₂₆Cu₇₄/Co₃O₄, and Co₃O₄.

Samples/ Binding Energy (eV)	Ir ₂₆ Cu ₇₄	Ir ₂₆ Cu ₇₄ /Co ₃ O ₄	Co ₃ O ₄
Ir ⁰ 4f 7/2	60.78	60.98	/
Ir ⁰ 4f 5/2	63.58	63.90	/
Ir ⁴⁺ 4f 7/2	61.87	61.88	/
Ir ⁴⁺ 4f 5/2	64.58	64.78	/
Cu ⁰ 2p 3/2	932.18	932.28	/
Cu ⁰ 2p 1/2	951.98	952.28	/
Cu ²⁺ 2p 3/2	933.98	934.88	/
Cu ²⁺ 2p 1/2	953.88	954.68	/
Co ²⁺ 2p 3/2	/	781.78	782.48
Co ²⁺ 2p 1/2	/	796.98	797.88
Co ³⁺ 2p 3/2	/	780.38	780.48
Co ³⁺ 2p 1/2	/	795.38	796.58

Table S3. OER performances of electrocatalysts in a 1.0 M KOH solution.

Catalysts	Electrolyte	OER(mV)@ <i>j</i> (mA/cm ²)	Tafel slope (mV·dec ⁻¹)	References
	1.0 M KOH	263.1@10		
Ir₂₆Cu₇₄	1.0 M KOH	283.1@20	82.3	This work
	1.0 M KOH	328.2@50		
	1.0 M KOH	264.9@10		
Ir₁₉Cu₈₁/Co₃O₄	1.0 M KOH	282.1@20	77.9	This work
	1.0 M KOH	310.9@50		
	1.0 M KOH	255.9@10		
Ir₂₆Cu₇₄/Co₃O₄	1.0 M KOH	268.1@20	67.5	This work
	1.0 M KOH	287.1@50		
	1.0 M KOH	256.1@10		
Ir₃₂Cu₆₈/Co₃O₄	1.0 M KOH	271.1@20	75.1	This work
	1.0 M KOH	296.5@50		
Ir-Co ₃ O ₄ @NC	1.0 M KOH	296.0@10	89.0	³
Pt ₃ Rh–Co ₃ O ₄ /C	1.0 M KOH	290 .0@10	63.4	⁴
5-Ir-NCO	1.0 M KOH	348.0@10	103.0	⁵
IrCo–N–C	0.1 M KOH	330.0@10	79.0	⁶
Ir-TrEGO	1.0 M KOH	338.0@10	127.7	⁷
IrO ₂ @Ir-MOF	1.0 M KOH	283.0@10	110.6	⁸

IrCo NRAs	1.0 M KOH	257.3@10	70.1	⁹
IrO ₂ /NF	1.0 M KOH	292.0@10	60.7	¹⁰
Ir nanochains	1.0 M KOH	340.0@10	125.0	¹¹

Table S4. OER performances of noble metal based electrocatalysts in a 0.5 M H₂SO₄ electrolyte.

Catalysts	Electrolyte	OER(mV)@ <i>j</i> (mA/cm ²)	Tafel slope (mV·dec ⁻¹)	References
Ir₂₆Cu₇₄	0.5 M H₂SO₄	387.0@10	296.4	This work
	0.5 M H₂SO₄	434.9@20		
Ir₁₉Cu₈₁/Co₃O₄	0.5 M H₂SO₄	334.9@10	191.8	This work
	0.5 M H₂SO₄	369.1@20		
Ir₂₆Cu₇₄/Co₃O₄	0.5 M H₂SO₄	293.0@10	165.3	This work
	0.5 M H₂SO₄	317.1@20		
Ir₃₂Cu₆₈/Co₃O₄	0.5 M H₂SO₄	317.0@10	182.9	This work
	0.5 M H₂SO₄	345.9@20		
IrO ₂ /Co ₃ O ₄	0.5 M H ₂ SO ₄	452.0@10	114.4	¹²
Ir ₁ -Co ₃ O ₄ -NS-300	0.5 M H ₂ SO ₄	505.0@10	129.3	¹³
IrCoO _x @LLCF	0.1 M HClO ₄	286 ± 5@10	47.3 ± 2	¹⁴
IrO ₂ @Co ₃ O ₄	0.5 M H ₂ SO ₄	301.0@10	72.1	¹⁵
IrCoNi PHNCs	0.5 M H ₂ SO ₄	309.0@10	/	¹⁶
Ir(20)/Fe@NCNT-900	0.5 M H ₂ SO ₄	300.0@10	64.5	¹⁷
Rh ₂₂ Ir ₇₈	0.5 M H ₂ SO ₄	300.0@10	/	¹⁸
HM-IrO ₂	0.5 M H ₂ SO ₄	312.0@10	61.2	¹⁹
C-IrO ₂	0.5 M H ₂ SO ₄	308.0@10	87.7	²⁰

Ir/G	0.5 M H ₂ SO ₄	389.0@10	126.6	²¹
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Table S5. ICP data of the Ir₂₆Cu₇₄/Co₃O₄ post OER in alkaline and acidic conditions.

Samples	C _{Ir} (mg/mL)	C _{Cu} (mg/mL)	C _{Co} (mg/mL)	Mole ration
Ir ₂₆ Cu ₇₄ /Co ₃ O ₄ (1.0 M KOH)	0.885	0.036	2.845	Ir ₈₉ Cu ₁₁
Ir ₂₆ Cu ₇₄ /Co ₃ O ₄ (0.5 M H ₂ SO ₄)	0.950	0.031	3.367	Ir ₉₁ Cu ₉

References

- 1 . Q. Zhang, W. Zhang, J. Zhu, X. Zhou, G. -R. Xu, D. Chen, Z. Wu, L. Wang, *Adv. Energy Mater.*, 2023, 2304546.
- 2 . J. Chen, Y. Ma, T. Huang, T. Jiang, S. Park, J. Xu, X. Wang, Q. Peng, S. Liu, G. Wang, W. Chen, *Adv. Mater.*, 2023, 2312369.
- 3 . S. Jung, R. A. Senthil, C. J. Moon, N. Tarasenka, A. Min, S. J. Lee, N. Tarasenka, M. Y. Choi, *Chem. Eng. J.*, 2023, 143717468.
- 4 . N. Bhuvanendran, C. W. Park, H. Su, S. Y. Lee, *Environ. Res.*, 2023, 115950229.
- 5 . H. -J. Lee, D. -H. Park, W. -J. Lee, S. -B. Han, M. -H. Kim, J. -H. Byeon, K. -W. Park, *Appl. Catal. A: Gen.*, 2021, 118377626.
- 6 . M. Xiao, J. Zhu, S. Li, G. Li, W. Liu, Y. -P. Deng, Z. Bai, L. Ma, M. Feng, T. Wu, D. Su, J. Lu, A. Yu, Z. Chen, *ACS Catal.*, 2021, 8837-884611.
- 7 . X. Li, J. Cao, J. Chen, Y. Zhu, H. Xia, Z. Xu, C. Gu, J. Xie, M. Jones, C. Lyu, J. Corbin, X. Li, W. Hu, *Adv. Funct. Mater.*, 2024, 231353034.
- 8 . L. Li, G. Li, Y. Zhang, W. Ouyang, H. Zhang, F. Dong, X. Gao, Z. Lin, *J. Mater. Chem. A*, 2020, 25687-256958.
- 9 . Y. Zhang, G. Zhang, M. Zhang, X. Zhu, P. Shi, S. Wang, A. -L. Wang, *Chem. Eng. J.*, 2022, 133577433.
- 10 . S. Hong, K. Ham, J. Hwang, S. Kang, M. H. Seo, Y. -W. Choi, B. Han, J. Lee, K. Cho, *Adv. Funct. Mater.*, 2023, 220954333.
- 11 . Z. Liu, J. Li, J. Zhang, M. Qin, G. Yang, Y. Tang, *ChemCatChem*, 2020, 3060-306712.
- 12 . K. Hua, R. Ding, X. Duan, Z. Rui, X. Li, Y. Wu, D. Yang, J. Li, J. Liu, *ACS Appl. Nano Mater.*, 2024, 487-4977.
- 13 . Y. Liu, Y. Chen, X. Mu, Z. Wu, X. Jin, J. Li, Y. Xu, L. Yang, X. Xi, H. Jang, Z. Lei, Q. Liu, S. Jiao, P. Yan, X. Li, R. Cao, *ACS Catal.*, 2023, 3757-376713.
- 14 . L. Chong, J. Wen, E. Song, Z. Yang, I. D. Bloom, W. Ding, *Adv. Energy Mater.*, 2023, 230230613.
- 15 . W. Han, Y. Qian, F. Zhang, Y. He, P. Li, X. Zhang, *Chem. Eng. J.*, 2023, 145353473.
- 16 . J. Feng, F. Lv, W. Zhang, P. Li, K. Wang, C. Yang, B. Wang, Y. Yang, J. Zhou, F. Lin, G. -C. Wang, S. Guo, *Adv. Mater.*, 2017, 170379829.
- 17 . Z. Zhang, Y. Xia, M. Ye, D. Wen, W. Zhang, W. Peng, L. Tian, W. Hu, *Int. J. Hydrg. Energy*, 2022, 13371-1338547.
- 18 . Z. Liu, Z. Kong, S. Cui, L. Liu, F. Wang, Y. Wang, S. Wang, S. -Q. Zang, *Small*, 2023, 230221619.
- 19 . J. Wu, W. Zou, J. Zhang, L. Zhang, H. Song, Z. Cui, L. Du, *Small*, 2024, 230841920.
- 20 . H. Yu, F. Liao, W. Zhu, K. Qin, J. Shi, M. Ma, Y. Li, M. Fang, J. Su, B. Song, L. Li, R.R. Zairov, Y. Ji, M. Shao, Q. Shao, *ChemCatChem*, 2023, e20230073715.
- 21 . S. Zhang, L. Yin, Q. Li, S. Wang, W. Wang, Y. Du, *Chem. Sci.*, 2023, 5887-589314.