

Supplementary Information

Yanrui Xu,^{a†} Wangjian Liu,^{b†} Zihang Xu,^b Yitong Zhou^{*a} and Xin-Yao Yu ^{*ab}

^aInstitutes of Physical Science and Information Technology

Anhui University

Hefei 230601, P. R. China

^bSchool of Materials Science and Engineering

Anhui University

Hefei 230601, P. R. China

*Corresponding Authors

*Email: yuxinyao@ahu.edu.cn

*Email: zhouyt@ahu.edu.cn

Chemicals: Zinc acetate dihydrate, cetrimonium bromide (CTAB), and potassium bicarbonate analytical grade were purchased from Macklin. Silver target (99.99% purity) and carbon paper were purchased from ZhongNuo Advanced Material (Beijing) Technology Co., Ltd and Suzhou Sinero Technology Co., Ltd, respectively. The CO₂ and Ar feed gases are 99.999% pure.

Materials characterizations: X-ray diffraction (XRD) patterns were obtained on PANalytical Empyrean. Scanning electron microscopy (SEM) images were acquired with a Zeiss Sigma 500 scanning electron microscope at an acceleration voltage of 3 kV. TEM and HRTEM images and spatially resolved elemental mapping images of samples

were obtained on JEOL F200 field emission transmission electron microscope. XPS measurements were performed on Thermo Fischer ESCALAB 250 Xi using Al K α radiation. The optical emission signal of plasma during magnetron sputtering was recorded by PG2000 high speed spectrometer (Idea Optics). The elemental contents of Ag and Zn were analyzed by ICP-AES (0~260AMU Plasma generator).

Preparation of Zn/CP: The Zn nanoplate array was deposited on the carbon paper (working area is 1*1 cm²) by applying multi-step current of -54 and -84 mA for each 3 s with 120 cycles. During the electrodeposition process, the KCl saturated Ag/AgCl and a Pt foil (1*1 cm²) electrodes were used as the reference and counter electrodes, respectively. The electrolyte was 0.46 mol/L zinc acetate dihydrate aqueous solution with 1 mmol of CTAB. After deposition, the prepared Zn was carefully cleaned with deionized water.

Preparation of Ag-Zn/CP: The as-prepared Zn/CP was used as substrate for magnetron sputtering of Ag nanoparticles. In a typical sputtering process, the plasma power, sputtering time, and Ar gas pressure is 50 W, 5 min, and 1.5 Pa, respectively. The gas flow rate was maintained at 25 sccm and the substrate rotation speed is 80 rpm. A series of Ag-Zn/CP with different loading of Ag were also prepared by adjusting the sputtering time.

Preparation of Ag/CP: The Ag/CP was obtained under the same sputtering parameters with Ag-Zn/CP except for replacing the substrate with bare carbon paper (working area is 1*1 cm²).

Electrochemical measurements: Various electrochemical characterizations were

conducted with an electrochemical workstation (IVIUM) in an H-type cell separated by a Nafion membrane (Nafion 117) and filled with 40 mL of 0.1 M KHCO₃ electrolyte in each side. In the three-electrode system, the as synthesized catalysts, KCl saturated Ag/AgCl and Pt foil (1*1 cm²) were used as the working, reference and counter electrodes, respectively. The electrolyte was saturated with CO₂ or Ar with a gas flow of 20 sccm for at least 30 min and the gas flow was maintained during the test. All potentials were measured against the Ag/AgCl reference electrode and converted to the RHE reference. 80% *iR* compensation was also performed. After 30 min of Chronopotentiometry (*i-t*) test, the main gas products (CO and H₂) were analyzed using directly connected gas chromatography (GC 9090II). The Faraday efficiencies (FEs) of CO and H₂ were calculated by $FE = N \cdot n \cdot F / Q$, where *N* (number of electrons exchanged) is 2 for CO₂ to CO and HER, *n* is the mole number of the product, F (Faraday constant) is 96485 C/mol, and *Q* is the total charge passed.

The electrochemically active surface area (ECSA) was estimated with the electrochemical double-layer capacitance (*C_{dl}*). A series of cyclic voltammetry (CV) curves were measured at different scan rates (10, 20, 40, 60, 80, and 100 mV s⁻¹) in a non-Faradaic region and the difference in current density between the anodic and cathodic sweeps (Δj) was plotted as a function of scan rates to fit a straight line with slope equal to *C_{dl}*.

In Situ FTIR Test: The in situ FTIR measurement was carried out on a Nicolet iS50 FT-IR spectrometer. During the measurement, the catalysts were coated on the surface of silicon crystal as working electrode. Ag/AgCl was used as reference electrode and Pt

wire was used as counter electrode. 0.1 M KHCO_3 was used as the reaction electrolyte. The flow rate of CO_2 was maintained at 20 sccm. Internal reflection mode was used to obtain in situ infrared data. The relevant spectral curves were acquired within 15 min during the *i-t* measurements.

DEMS test: The DEMS test was performed by HPR-40 mass spectrometer. Similar to the In situ FTIR measurement, the catalysts, the Ag/AgCl, and the Pt wire served as working, reference and counter electrode, respectively. The electrolyte was also 0.1 M KHCO_3 with CO_2 continuously bubbling. When the baseline was smooth, the *i-t* test (-0.9 V vs. RHE) was performed to obtain the signals of various substances.

Methods of DFT calculation: All the first-principle density functional theory (DFT) calculations were carried out using Vienna Ab-initio Simulation Package (VASP) with version of 6.2.1¹⁻³. The Perdew-Burke-Ernzerh (PBE) in the generalized gradient approximation (GGA) was applied to describe the exchange-correlation potential^{4,5}. Based on the plane wave method, the projector augmented-wave (PAW) method with an energy cutoff of 400 eV was implemented to expand the valence electrons^{6,7}. The implicit self-consistent electrolyte model provided by VASPsol code has been used to consider the influence of aqueous solution and co-adsorbed H_2O^* on the energy of CO_2RR and HER intermediates.^{8,9} The Langmuir-Hinshelwood (L-H) mechanism was used to calculate the CO_2RR pathway.

All structures were fully relaxed until the electronic energy and force acting on atom were smaller than 10^{-5} eV and $0.02 \text{ eV} \cdot \text{\AA}^{-1}$, respectively. The Brillouin-zone sampling were conducted using Monkhorst-Pack (MP) grids of special points with the

separation of $0.04 \text{ \AA}^{-1}$. A Gaussian smearing of 0.05 eV was applied to speed up self-consistent field iteration. The 4-layer 4×4 supercell of Zn (001) and 2×2 supercell of AgZn_3 (002) was used to build the slab surface model and the bottom two layers were fixed while other atoms are fully relaxed. A vacuum height of $15 \text{ \AA}$ along the vertical direction was selected to avoid the unwanted interaction between the slab and its period images. All the optimized configurations and the electron localization function (ELF) distribution were illustrated with VESTA software¹⁰.

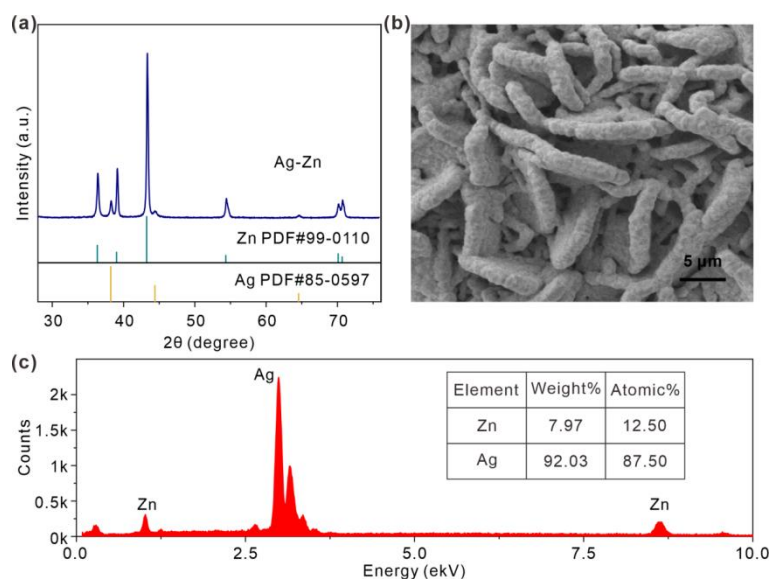


Fig. S1 (a) XRD pattern, (b) SEM image, and (c) EDS spectrum of Ag-Zn/CP.

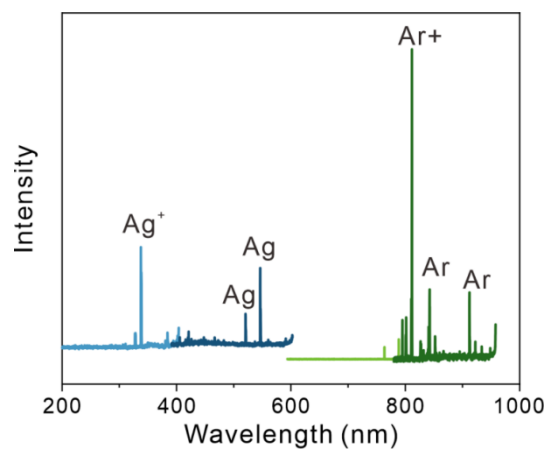


Fig. S2 Optical emission spectrum during magnetron sputtering (Plasma power: 50 W, Gas pressure: 1.5 Pa).

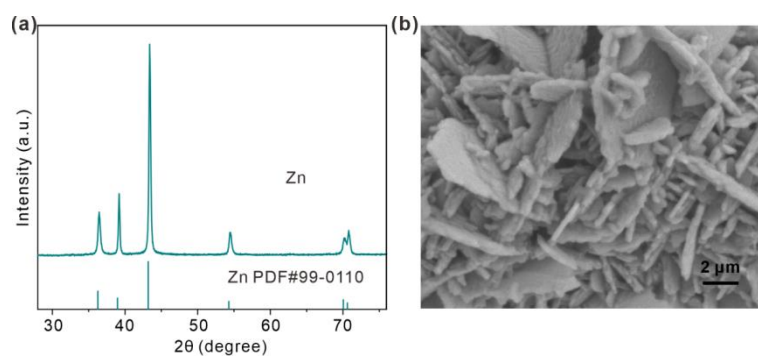


Fig. S3 (a) XRD pattern and (b) SEM image of Zn/CP.

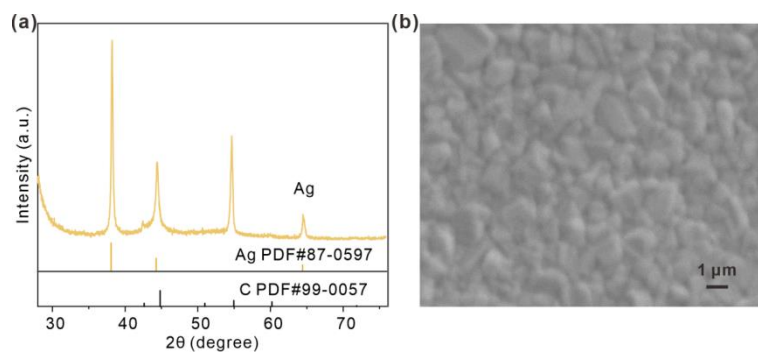


Fig. S4 (a) XRD pattern and (b) SEM image of the Ag/CP.

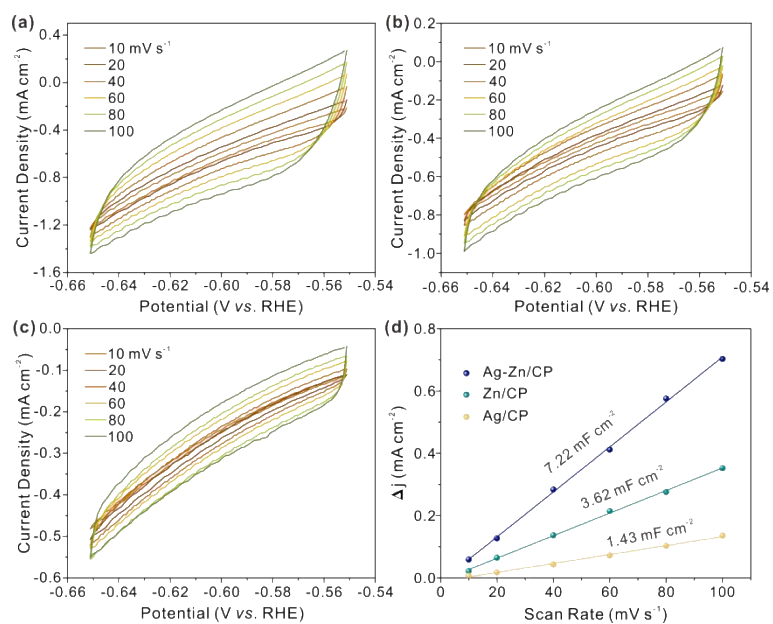


Fig. S5 CV curves of (a) Ag-Zn/CP, (b) Zn/CP, and (c) Ag/CP at different scan rates (10, 20, 40, 60, 80, and 100 mV s^{-1}); (d) Functions of the current density differences vs. scan rates at -0.60 V vs. RHE.

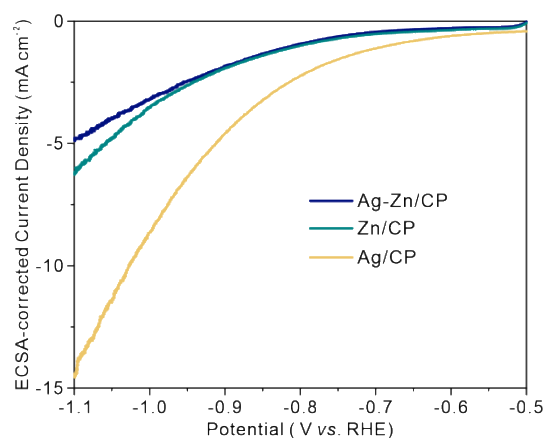


Fig. S6 The ESCA normalized LSV curves of Ag-Zn/CP, Zn/CP, and Ag/CP.

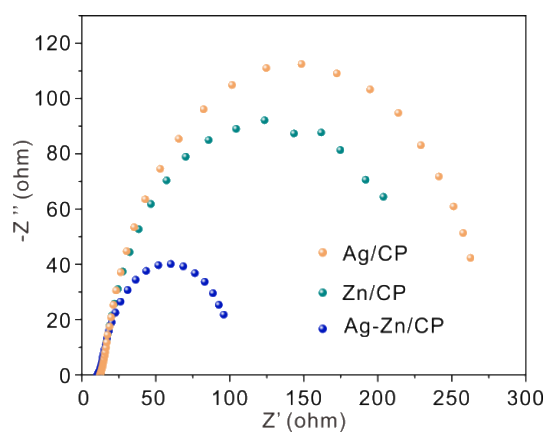


Fig. S7 Nyquist plots of Ag-Zn/CP, Zn/CP, and Ag/CP.

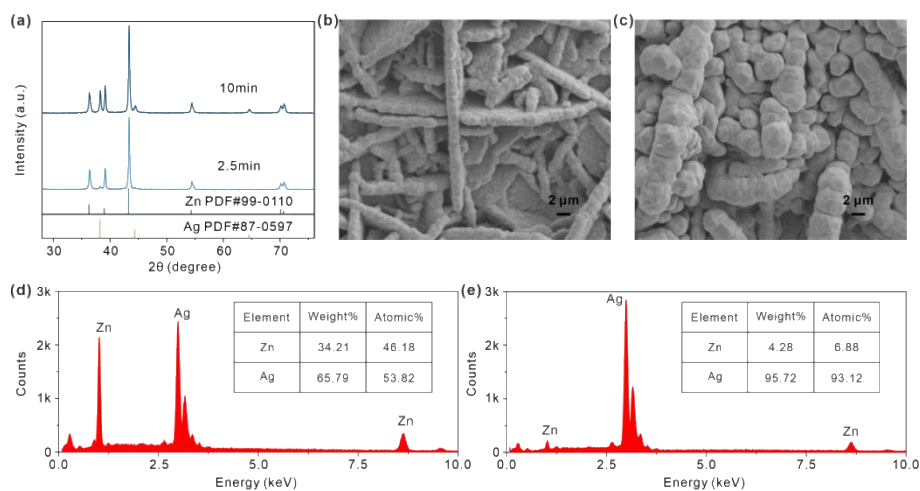


Fig. S8 (a) XRD patterns of samples obtained at different sputtering time; (b,c) SEM images of the samples obtained at the sputtering time of 2.5 min (b) and 10 min (c); (d,e) EDS spectra of the samples obtained at the sputtering time of 2.5 min (d) and 10 min (e).

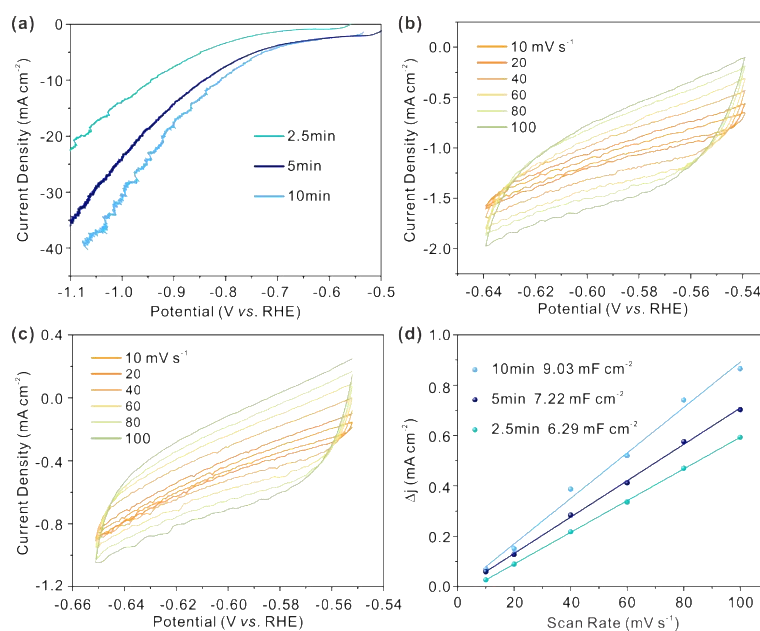


Fig. S9 (a) LSV curves and (d) Plots of the current density differences at -0.60 V vs. scan rates; (c,d) CV curves of samples obtained at the sputtering time of 2.5 min (c) and 10 min (d) at different scan rates (10, 20, 40, 60, 80, and 100 mV s⁻¹).

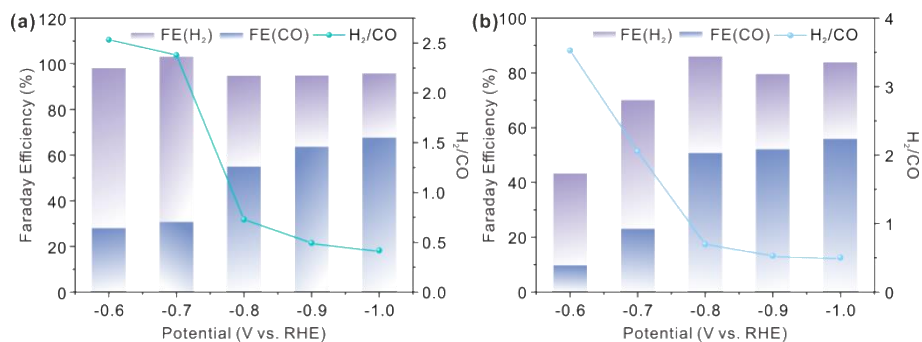


Fig. S10 FE and syngas ratio of the samples obtained at the sputtering time of 2.5 min (a) and 10 min (b).

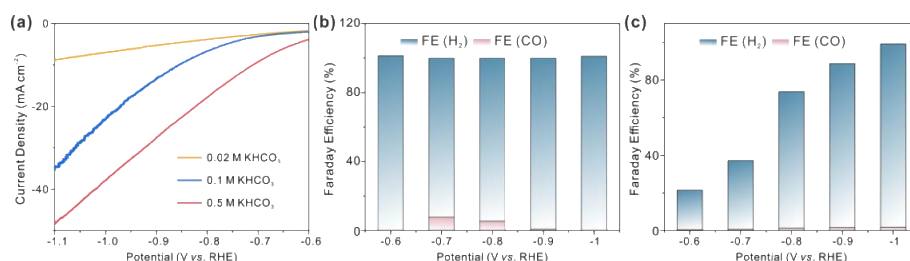


Fig. S11 (a) LSV curves of Ag-Zn/CP in CO₂-saturated KHCO₃ with different concentrations; FE in (b) 0.5 M KHCO₃ and (c) 0.02 M KHCO₃.

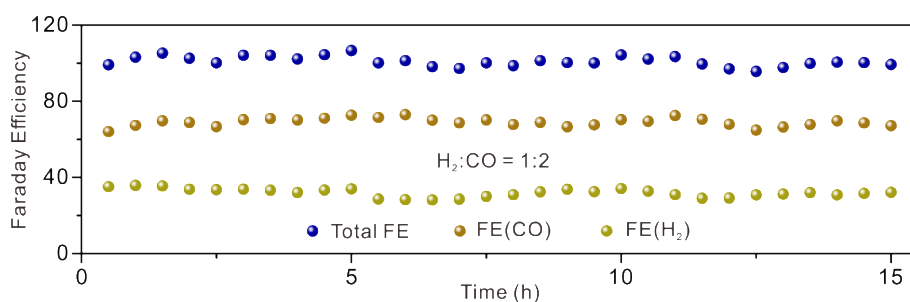


Fig. S12 Time-dependent FEs of CO and H₂ for Ag-Zn/CP at -0.9 V vs. RHE.

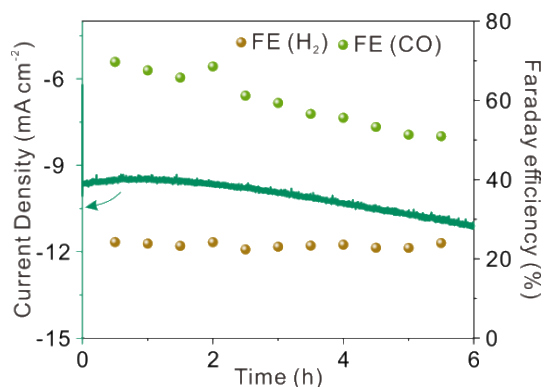


Fig. S13 Time-dependent current density and FEs of CO as well as H₂ for Zn/CP at -0.9 V vs. RHE.

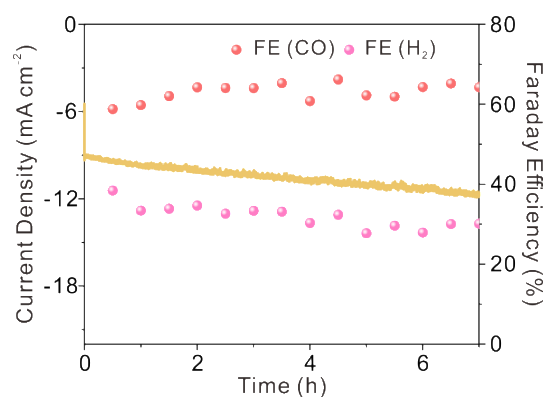


Fig. S14 Time-dependent current density and FEs of CO as well as H₂ for Ag/CP at -0.9 V vs. RHE.

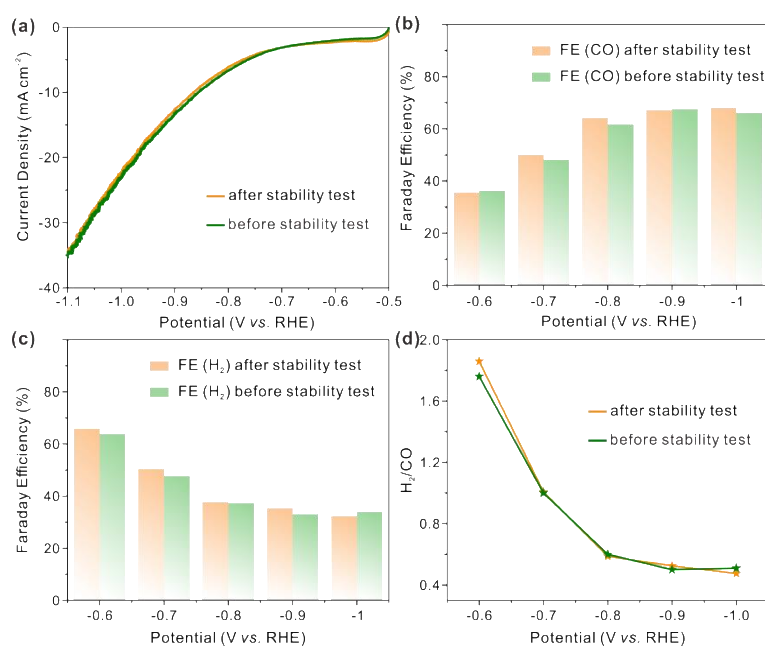


Fig. S15 (a) LSV curves and (b-d) FE (CO), FE (H₂), and H₂/CO ratios of Ag-Zn/CP catalyst before and after stability test.

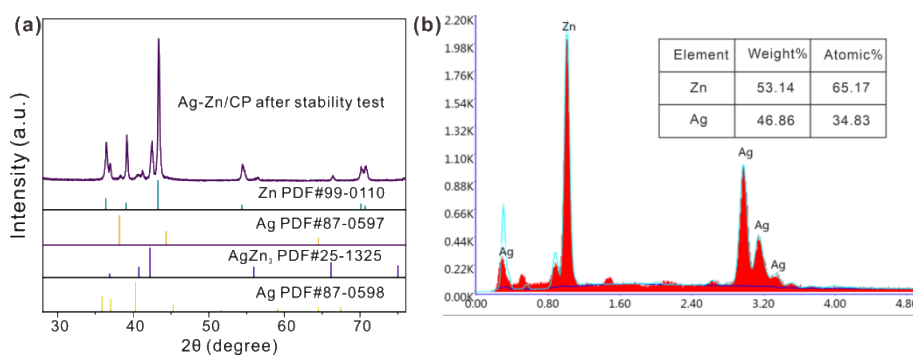


Fig. S16 (a) XRD pattern and (b) EDS spectra of Ag-Zn/CP after stability test. A very small amount of new phased Ag (PDF#87-0598) can be also found.

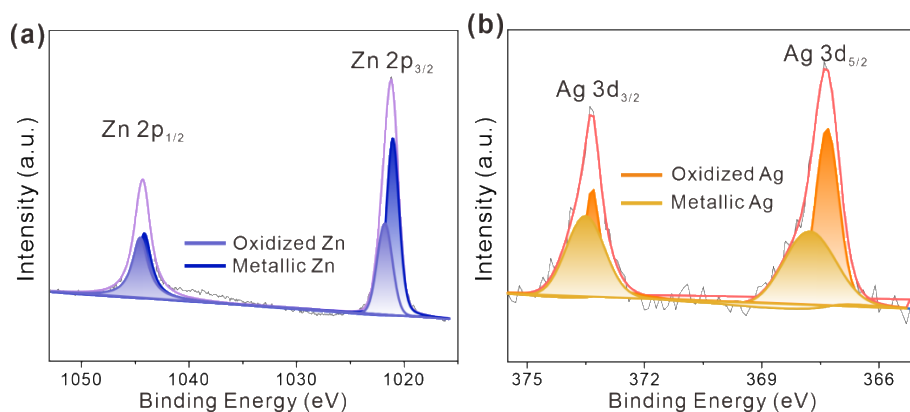


Fig. S17 (a) Zn 2p and (b) Ag 3d XPS spectra of Ag-Zn/CP after stability test. The presence of oxides may be due to the surface oxidation of the tested sample when exposed to air.

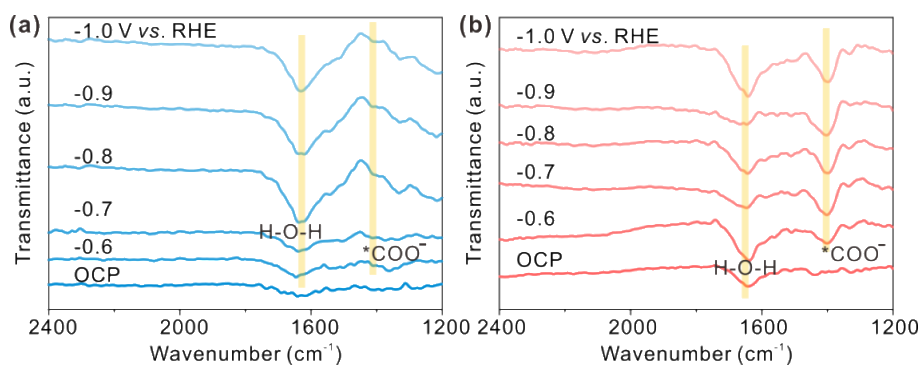


Fig. S18 In-situ FTIR spectra of (a) Zn/CP and (b) Ag/CP at different potentials; Time-dependent in-situ FTIR spectra of (c) Zn/CP and (d) Ag/CP at -0.9 V vs. RHE.

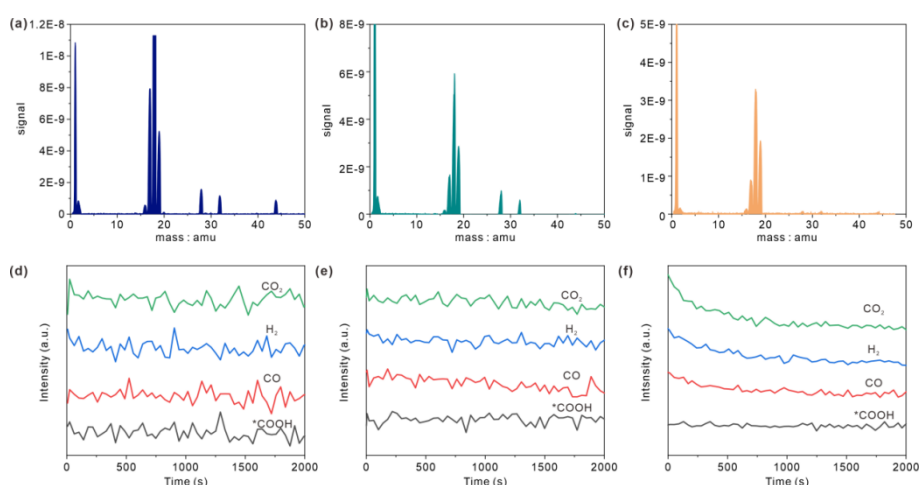


Fig. S19 DEMS detection of various species for (a) Ag-Zn, (b) Zn, and (c) Ag; Mass spectrum of CO₂, H₂, CO, and *COOH for (c) Ag-Zn, (d) Zn, and (e) Ag.

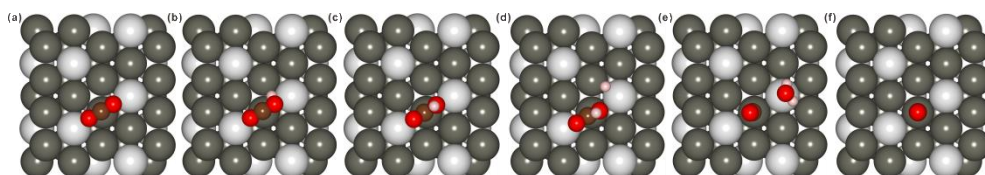


Fig. S20 Top views of (a) $^*\text{CO}_2$, (b) $^*\text{CO}_2+^*\text{H}$ (c) $^*\text{COOH}$, (d) $^*\text{COOH}+^*\text{H}$ (e) $^*\text{CO}+\text{H}_2\text{O}^*$ and (f) $^*\text{CO}$ on the AgZn_3 . The pink, red, brown, dark gray, and white gray spheres represent H, O, C, Zn, and Ag atoms, respectively.

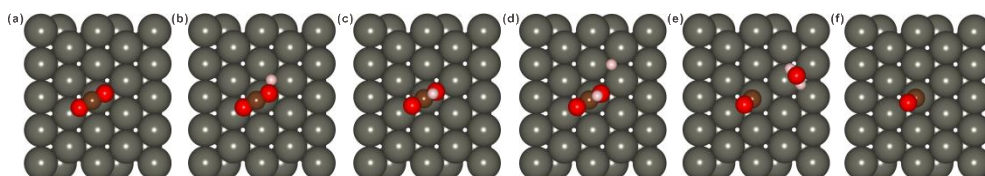


Fig. S21 Top views of (a) $^*\text{CO}_2$, (b) $^*\text{CO}_2+^*\text{H}$ (c) $^*\text{COOH}$, (d) $^*\text{COOH}+^*\text{H}$ (e) $^*\text{CO}+\text{H}_2\text{O}^*$ and (f) $^*\text{CO}$ on the Zn. The pink, red, brown, dark gray, and white gray spheres represent H, O, C, Zn, and Ag atoms, respectively.

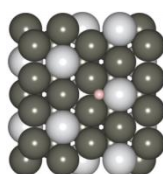


Fig. S22 Top view of $^*\text{H}$ on the AgZn_3 . The pink, dark gray, and white gray spheres represent H, Zn, and Ag atoms, respectively.

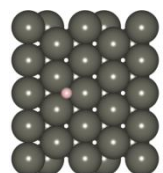


Fig. S23 Top view of $^*\text{H}$ on the Zn. The pink and dark gray spheres represent H and Zn atoms, respectively.

Table S1. Selected some high-performance electrocatalysts for CO₂RR reported in the literature. As can be seen, few catalysts can regulate the proportion of synthesis gas at 1:1~2:1 or 1:3.3~1:2 for H₂/CO.

Catalyst	Electrolyte	Activity		Selectivity		Ref.
		Potential (V vs. RHE)	Current Density (mA cm ⁻²)	Potential (V vs. RHE)	H ₂ /CO	
Ag-Zn/CP	0.1 M KHCO ₃	-1.1	35.4	-0.6	2:1	This work
				-0.7	1:1	
				-0.9	1:2	
Co ₃ O ₄ -CDots-C ₃ N ₄	0.5 M KHCO ₃	-1.1	<30	-0.45 and -0.75	1:1	S 9
Cu/In ₂ O ₃	0.1 M KHCO ₃	-1.2	~20	-0.7 to -1.1	2:1	S 10
Defective Sn-Zn perovskites	0.1 M KHCO ₃	-1.2	<15	-1.1	2:1	S 11
AgP ₂	0.1 M KHCO ₃	-1.2	~22.5	-1.0	1:5	S 12
Zn-Ln dual atomic catalysts	0.5 M KHCO ₃	-1.5	<4	-1.5	2:1	S 13
Ni-doped ZnO	0.1 M KHCO ₃	-1.8	25.04	-1.4	1:0.04	S 14
Zn _x Cd _{1-x} S-Amine	0.5 M NaHCO ₃	-1.1	<25	-1.06 to -1.16	2:3	S 15
N-doped tubular carbon foam (CF-120)	0.1 M KHCO ₃	-1.3	<20	-0.5	1:2	S 16
CdS _x Se _{1-x}	0.1 M NaHCO ₃	-1.2	27.1	-1.2	1:4 to 4:1(x from 1 to 0)	S 17
Bi/Zn Dual Single-Atom Catalysts	0.5 M KHCO ₃	-1.2	<15	-0.7	~1:1	S18

Table S2. Concentration of silver and zinc elements in electrolyte determined by ICP-AES.

Elements	Concentration (ug/L)
Ag	0.16
Zn	1386.4

Reference

1. G. Kresse, J. Hafner, Phys. Rev. 1993, 47, 558.
2. G. Kresse, J. Furthmuller, Phys. Rev. 1996, 54, 11169.
3. G. Kresse, J. Furthmuller, Comput. Mater. Sci. 1996, 6, 15.
4. J. P. Perdew, Y. Wang, Phys. Rev. B 1992, 45, 13244.
5. J. P. Perdew, K. Burke, Phys. Rev. Lett. 1996, 77, 3865.
6. P. E. Blöchl, Phys. Rev. B 1994, 50, 17953.
7. G. Kress, D. Joubert, Phys. Rev. B 1999, 59, 1758.
8. K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T. A. Arias and R. G. Hennig, *J. Chem. Phys.*, 2014, 140, 084106.
9. K. Mathew, V. S. C. Kolluru, S. Mula, S. N. Steinmann and R. G. Hennig, *J. Chem. Phys.*, 2019, 151, 234101.
10. K. Momma, Izumi, F. J. Appl. Crystallogr. 2011, 44, 1272.
9. S. Guo, S. Zhao, X. Wu, H. Li, Y. Zhou, C. Zhu, N. Yang, X. Jiang, J. Gao, L. Bai, Y. Liu, Y. Lifshitz, S. T. Lee and Z. Kang, Nat. Commun. 2017, 8, 1828.
10. J. Shen, L. Wang, X. He, S. Wang, J. Chen, J. Wang and H. Jin, ChemSusChem 2022, 15, e202201350.
11. J. Jiang, B. Huang, R. Daiyan, B. Subhash, C. Tsounis, Z. Ma, C. Han, Y. Zhao, L. H. Effendi, L. C. Gallington, J. N. Hart, J. A. Scott and N. M. Bedford, Nano Energy 2022, 101, 107593-107605.
12. H. Li, P. Wen, D. S. Itanze, Z. D. Hood, X. Ma, M. Kim, S. Adhikari, C. Lu, C. Dun, M. Chi, Y. Qiu and S. M. Geyer, Nat. Commun. 2019, 10, 5724.
13. Z. Liang, L. Song, M. Sun, B. Huang and Y. Du, Sci. Adv. 2021, 7, eabl4915.
14. J. Wang, Q. Xiang, W. Zhang, F. Shi, F. Li, P. Tao, C. Song, W. Shang, T. Deng and J. Wu, ACS Appl. Energy Mater. 2022, 5, 5531-5539.
15. N. Meng, C. Liu, Y. Liu, Y. Yu and B. Zhang, Angew. Chem. Int. Ed. 2019, 58, 18908-18912.
16. H. Li, N. Xiao, Y. Wang, C. Li, X. Ye, Z. Guo, X. Pan, C. Liu, J. Bai, J. Xiao, X. Zhang, S. Zhao and J. Qiu, J. Mater. Chem. A 2019, 7, 18852-18860.
17. R. He, A. Zhang, Y. Ding, T. Kong, Q. Xiao, H. Li, Y. Liu and J. Zeng, Adv. Mater.

2018, 30, 1705872.

18. L. Meng, E. Zhang, H. Peng, Y. Wang, D. Wang, H. Rong and J. Zhang, ChemCatChem 2022, 14,e202101801.