Electronic Supplementary Information (ESI)

Elaborate tree-like Cu-Ag clusters from green electrodeposition for efficiently electrocatalyzing CO$_2$ into syngas

Cuiping Xu[a], Yuande Shi[a,b], Xiaohuan Zou[a], Hongyang Xu[a], Lingxing Zeng[a, c*],

Zhongshui Li[a, b, c, d*],   Qiufeng Huang[a,d]

[a] College of Chemistry & Materials Science, Fujian Normal University, Fuzhou 350007, China

[b] Fujian Province-Indonesia Marine Food Joint Research and Development Center Fuqing 350300, China

[c] College of Environmental and Resource Sciences, Fujian Normal University, Fuzhou 350007, China

[d] Fujian Key Laboratory of Polymer Materials, Fujian Normal University, Fuzhou 350007, China

[*] Corresponding author:

E-mail address: zsli@fjnu.edu.cn (Z.S. Li); zenglingxing@fjnu.edu.cn (L.X. Zeng)

Experimental section

1. Materials

C$_2$H$_5$OH ($\geq$ 99.7%), KHCO$_3$ ($\geq$ 99.5%), Cu(NO$_3$)$_2$ · 3H$_2$O ($\geq$ 99.0%), AgNO$_3$ ($\geq$ 99.8%) and polyvinylpyrrolidone (PVP, C$_6$H$_9$NO)$_n$) were all analytical reagents and purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). D$_2$O (99.9%), HCOOH (> 99%) and C$_2$H$_6$OS ($\geq$ 99.95%) were purchased from Aladdin Co. Ltd. (Shanghai, China). Nafion 117 solution (5%) was purchased from Sigma-Aldrish Co. Inc. (USA). The water used in all experiments was purified to a resistivity of 18.25 MΩ cm and deoxygenated with high purity nitrogen before use.

2. Characterization methods

X'pert Pro X-ray diffractometer (PANalytical, NED) was employed to record X-ray diffraction (XRD) patterns using Cu Kα radiation between 5° and 90° 2θ at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) was conducted on ESCALAB Xi+ electron spectrometer (Thermo Fisher Scientific, USA) using Al Kα radiation to investigate the surface valance states of samples. Specifically, the spectra were excited using with an Al-Kα radiation source (1486.6 eV) and binding energy was referenced to C1s peak at 284.8 eV. The software "XPSPEAK (Version 4)" was used to treat curve fitting based on a non-linear least-square regression method and linear type background corrections. The morphologies of catalysts were observed by high-resolution transmission electron microscopy (HRTEM), high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) and the element mappings, which

were conducted on TECNAI G2 transmission electron microscope (TEM, FEI, USA). It was also analyzed by scanning electron microscopy (SEM, Zeiss Sigma 500, Germany) to intuitively observe the surface morphology of as-electrodeposited Cu/Ag particles.

3. Electrochemical measurements

The entire CO_2RR electrochemical tests were carried out in a typical H-type electrolytic cell separated by Nafion 117 ion exchange membrane with 0.5 M $KHCO_3$ solution as electrolyte. Chenhua CHI650E electrochemical workstation (Shanghai, China) and three-electrode system were employed. As-electrodeposited carbon paper, Ag/AgCl electrode and platinum electrode were used as the working electrode, the reference electrode and the counter electrode, respectively. Before electrocatalytic CO_2RR, high-purity CO_2 (99.999%) was imported into the cathode chamber for 30 minutes to saturate the electrolyte. During the electrolysis process, CO_2 continuously bubbled at a flow rate of 20 mL min^{-1}, and constant magnetic stirring was maintained. Linear sweep voltammetry (LSV) test was performed in a 0.5 M $KHCO_3$ solution saturated with CO_2 at a sweep rate of 10 mV s^{-1} to obtain the onset potential. Chronoamperometry tests at the selected potential were carried out for 3600 s or 18000 s. The electrochemically active surface area (ECSA) was measured by the electric double layer capacitance (Cdl) method. The Cdl can be calculated from the CV curves in 0.5 M $KHCO_3$ solution. The formula is ECSA = Cdl $\times$ Z, and Z is a constant. Generally, a series of CV tests with different scan rates (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV s^{-1}) in the non-Faraday effect potential range was selected to calculate

Cdl which was directly related with ECSA. Electrochemical impedance spectra (EIS) were performed in 0.5 M $KHCO_3$ solution under open circuit voltage with frequency range of 100 kHz to 0.1 Hz, and Nyquist curve is obtained by applying different potentials. Especially, after fitting by an equivalent circuit, the semicircle diameter in Nyquist curve represents the charge-transfer resistance of catalyst (Rct). The potentials in this article have been converted into reversible hydrogen electrode (RHE), and the conversion formula is *E (vs. RHE) = E (vs. Ag/AgCl) + 0.21 + 0.0591 × pH* [1-2].

4. Reduction products measurements

The gas products produced from electrocatalytic reduction of CO_2 were quantitatively analyzed on line by gas chromatography (GC, FL9790Π, Fuli Analytical Instruments Co., Ltd, China). Flame ionization detector (FID) was used to detect the products such as CO, CH_4 and C_2H_4, and thermal conductivity detector (TCD) was used to detect H_2. The liquid product was analyzed by nuclear magnetic resonance spectroscopy (NMR, Buker 400MHz, Brook Company, Switzerland). The specific operation is as follows: 0.5 mL cathode electrolyte was mixed with 0.1 mL D_2O and 5 uL dimethyl sulfoxide (DMSO) solution, in which DMSO was used as internal standard for qualitative analysis and quantitative calculation. The Faradaic efficiency (FE) calculation formula is as follows: *FE=z n F / Q ✗ 100%* [3]. Among them, z is the number of electrons transferred, and the number of electrons transferred to generate HCOOH, CO and H_2 are all 2; n denotes the number of moles of the specific product, obtained by GC or NMR quantitative analysis; F is the Faradaic constant (96485 C mol^{-1}); Q is the total charge (C) consumed by the electrolysis process.
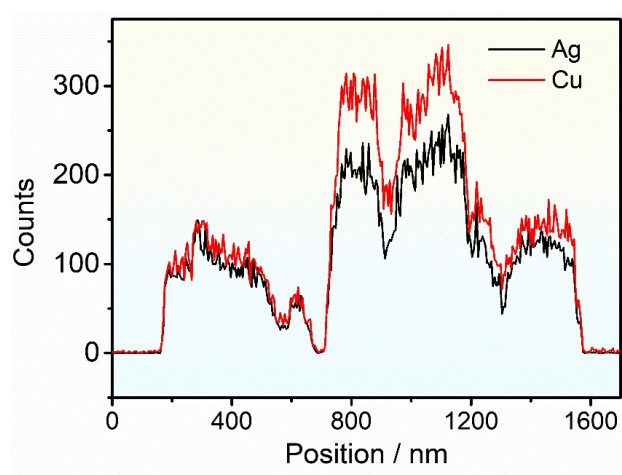
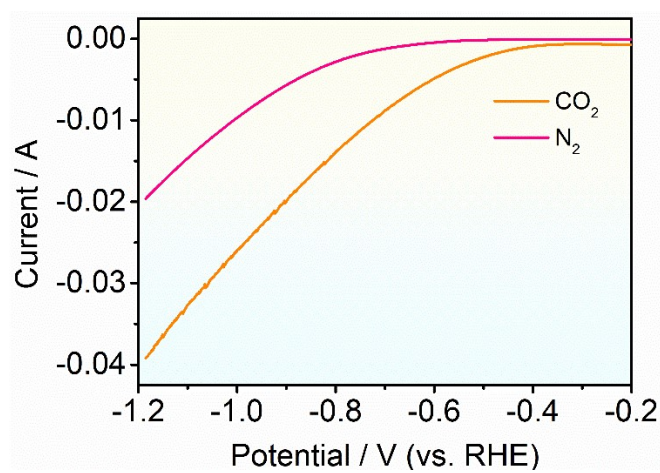Fig. S1 Element linear distribution of Cu & Ag along the cross-sectional line in Fig. 2j.

Fig. S2 LSV curves of Cu-Ag/CF in 0.5 M KHCO$_3$ solution
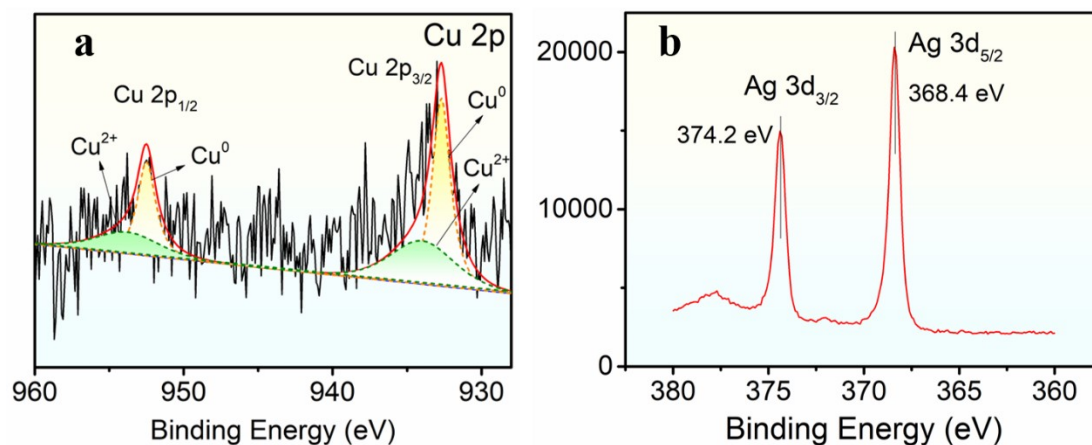
saturated with CO$_2$ or N$_2$.

Fig. S3 XPS spectra of Cu-Ag/CF after electrocatalytic tests: (a) Cu 2P XPS profile;
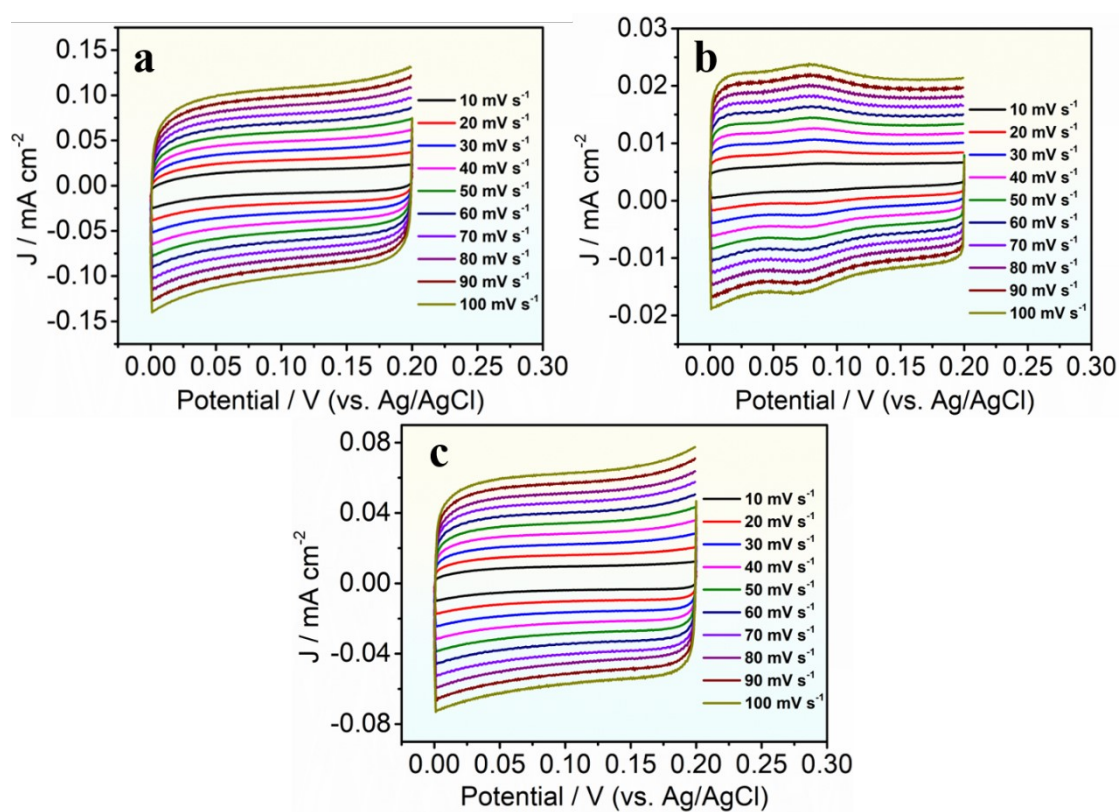
(b) Ag 3d XPS profile.

Fig. S4 CV curves at different scanning rate. (a) Cu-Ag/CF, (b) Cu/CF and (c) Ag/CF

Table S1. Comparison of electrocatalytic properties with the reported copper or silver based CO_2RR catalysts.

Catalysts	E / V (vs. RHE)	J_{co} / mA cm^{-2}	Highest FE/%	References
Cu-Ag/CF	-0.836	-7.03	80	This Work
Ag11@100-O	-1.4	-1.5	25.6	[4]
AgZn	-1.0	-2.97	84.2	[5]
Cu/Ag(S)	-1.4	-6.1	78.6	[6]
Ag@Cu	-1.06	-3.1	82	[7]
Cu$_{50}$Ag$_{50}$	-0.9	-4.88	80.25	[8]
o-Ag$_2$O	-0.95	-1.5	70	[9]

References

1. X. Sun, C. Chen, S. Liu, S. Hong, Q. Zhu, Q. Qian, B. Han, J. Zhang, L. Zheng, *Angew Chem Int Ed Engl*, 2019, **58**, 4669-4673.

2. E.B. Nursanto, W. Da Hye, M.S. Jee, H. Kim, N.-K. Kim, K.D. Jung, Y.J. Hwang, B.K. Min, *Top. Catal.*, 2017, **61**, 389-396.

3. Y. Wu, S. Cao, J. Hou, Z. Li, B. Zhang, P. Zhai, Y. Zhang, L. Sun, *Adv. Energy Mater.*, 2020, **10**, 2000588.

4. F. Mattarozzi, N. Visser, J.W. de Rijk, P. Ngene, P. de Jongh, *Eur. J. Inorg. Chem.*, 2022, **2022**, e20220036.

5.   W. Guo, K. Shim, Y.T. Kim, *Appl. Surf. Sci.*, 2020, **526**, 146651.

6.   Z. Ma, T. Wan, D. Zhang, J.A. Yuwono, C. Tsounis, J. Jiang, Y.H. Chou, X. Lu, P.V. Kumar, Y.H. Ng, D. Chu, C.Y. Toe, Z. Han, R. Amal, *ACS Nano*, 2023, **17**, 2387-2398.

7.   Z.Y. Chang, S.J. Huo, W. Zhang, J.H. Fang, H.L. Wang, *J. Phys. Chem. C*, 2017, **121**, 11368-11379.

8.   T. Zhang, Y. Liu, C. Yang, L. Tian, Y. Yan, G. Wang, *J. Alloys Compd.*, 2023, **947**, 169638.

9.   M. Yang, J.Z. Zhang, Y.Y. Cao, M.F. Wu, K. Qian, Z.H. Zhang, H.Y. Liu, J.G. Wang, W. Chen, W.X. Huang, *ChemCatChem*, 2018, **10**, 5128-5134.