Supplementary Information

# Mechanically mixing copper and silver into self-supporting electrocatalyst for hydrogen evolution

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**Fig. S1.** HER properties of Cu–*x*Ag samples with P-Cu as the reference: (a) LSV curves; (b) overpotentials at 10 mA/cm2.



**Fig. S2.** HER properties of Cu plate, P-Cu, and Cu–4Ag: (a) LSV curves; (b) overpotentials at 10 mA/cm2.



**Fig. S3.** CV curves of (a) Cu plate, (b) P-Cu, and (c) Cu–4Ag.

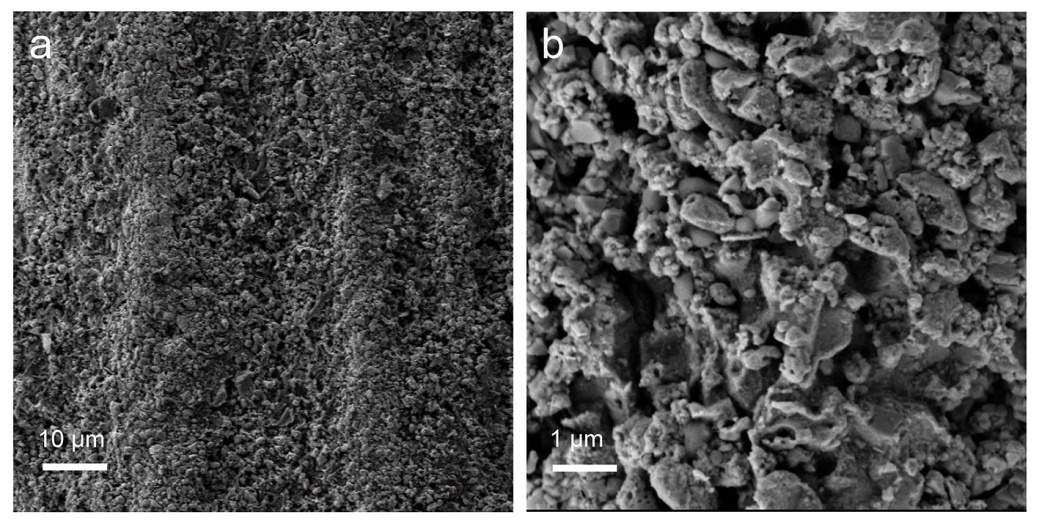
The number of active sites on different catalysts can be determined from Fig. S3, with values of 1.50×10−9, 1.16×10−8, and 1.30×10−8 mol/cm2 for Cu plate, P-Cu, and Cu–4Ag samples, respectively.



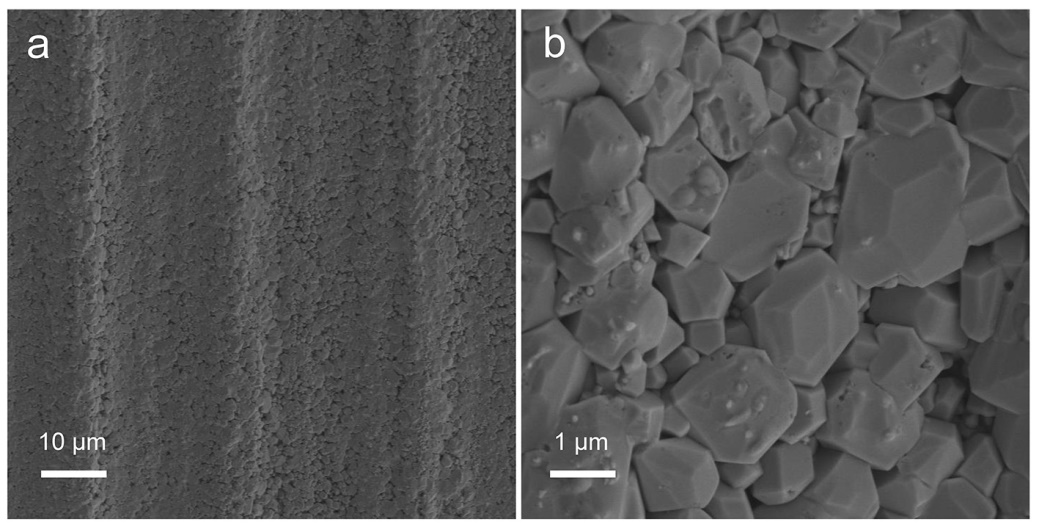
**Fig. S4.**  HER polarization curves of Cu–4Ag before and after stability test.



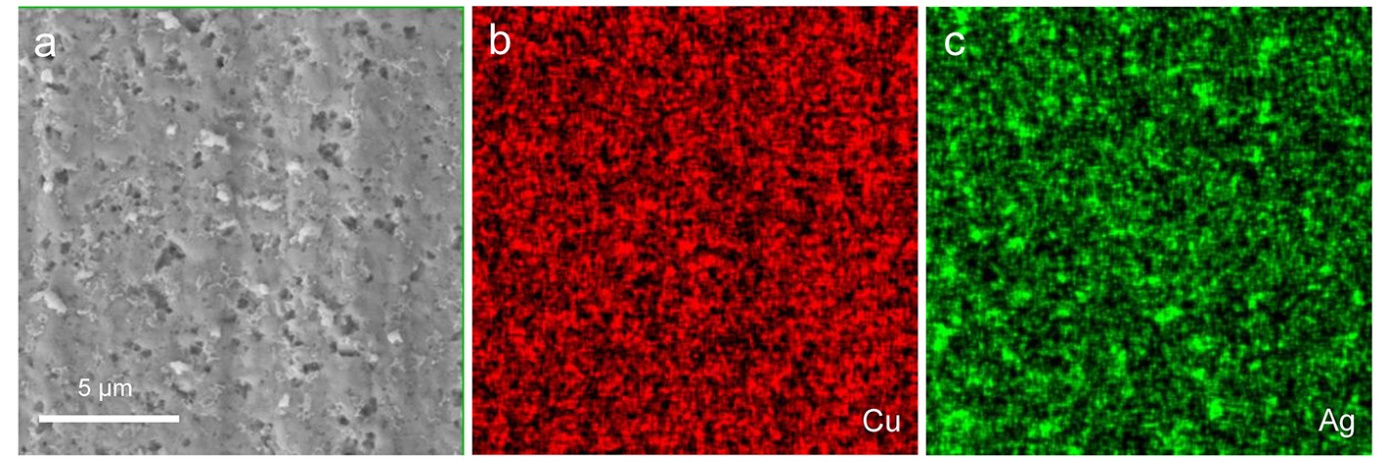
**Fig. S5.** XRD patterns of P-Cu, Cu–1Ag, Cu–2Ag, Cu–3Ag, and Cu–4Ag: (a) survey spectra and (b) the enlarged area around Cu (111) peak.



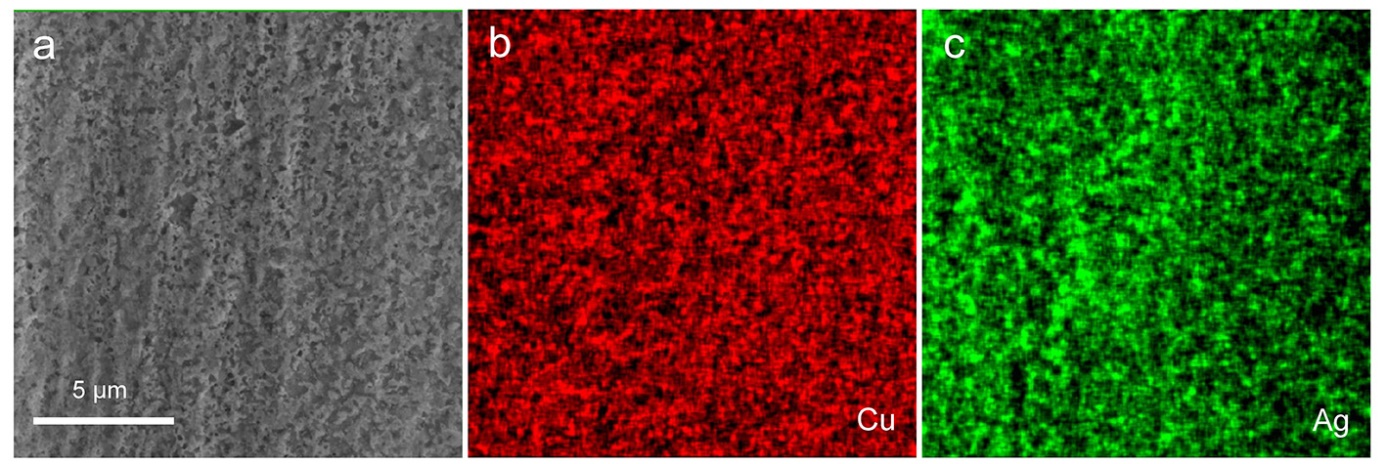
**Fig. S6.** SEM images of Cu–4Ag: (a) low magnification and (b) high magnification images.



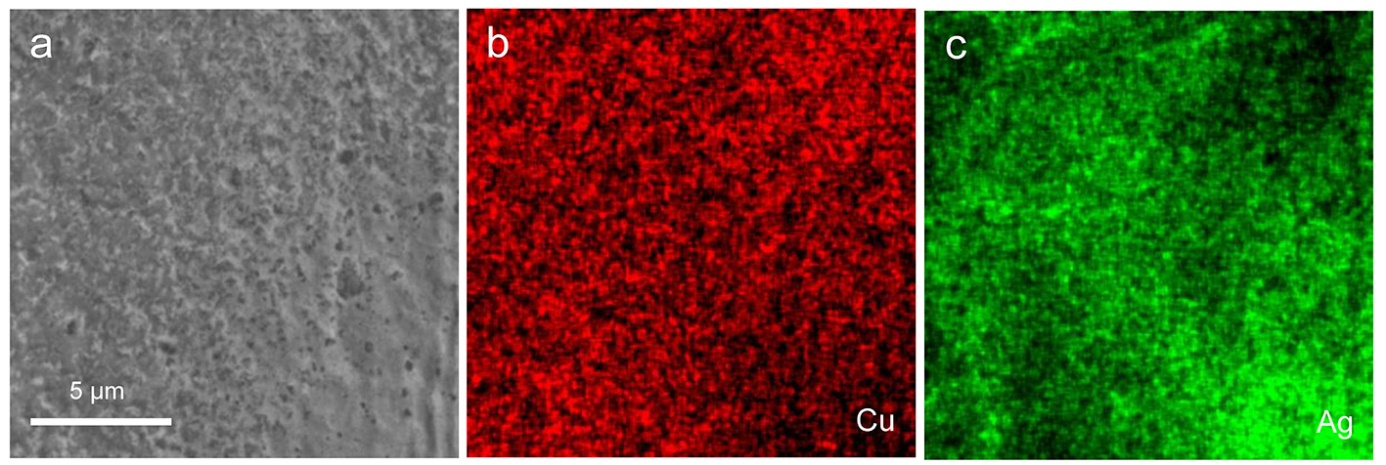
**Fig. S7.** SEM images of P-Cu: (a) low magnification and (b) high magnification images.



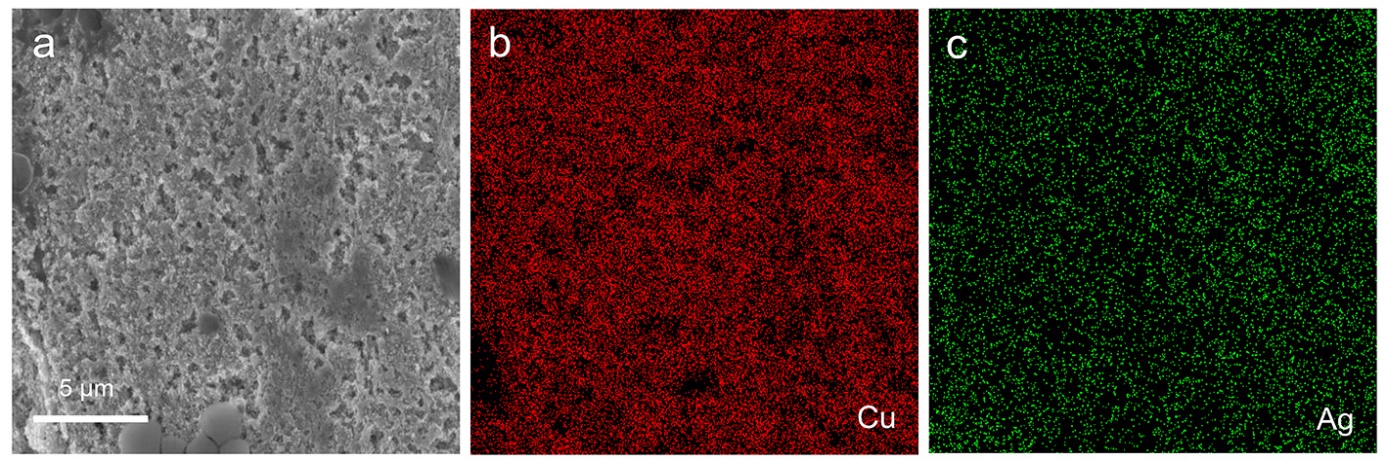
**Fig. S8.**  (a) SEM image of Cu–1Ag. (b) and (c) are the EDS elemental mapping of Cu and Ag, respectively.



**Fig. S9.** (a) SEM image of Cu–2Ag. (b) and (c) are the EDS elemental mapping of Cu and Ag, respectively.



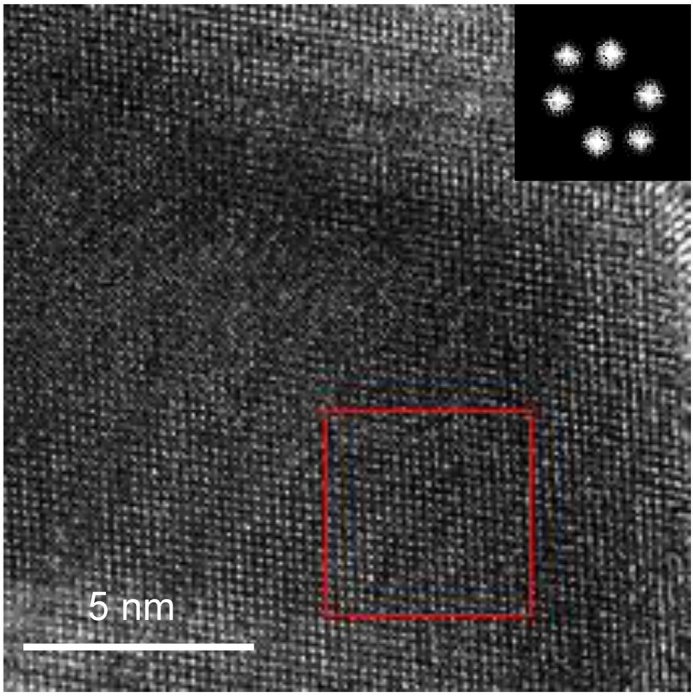
**Fig. S10.** (a) SEM image of Cu–3Ag. (b) and (c) are the EDS elemental mapping of Cu and Ag, respectively.



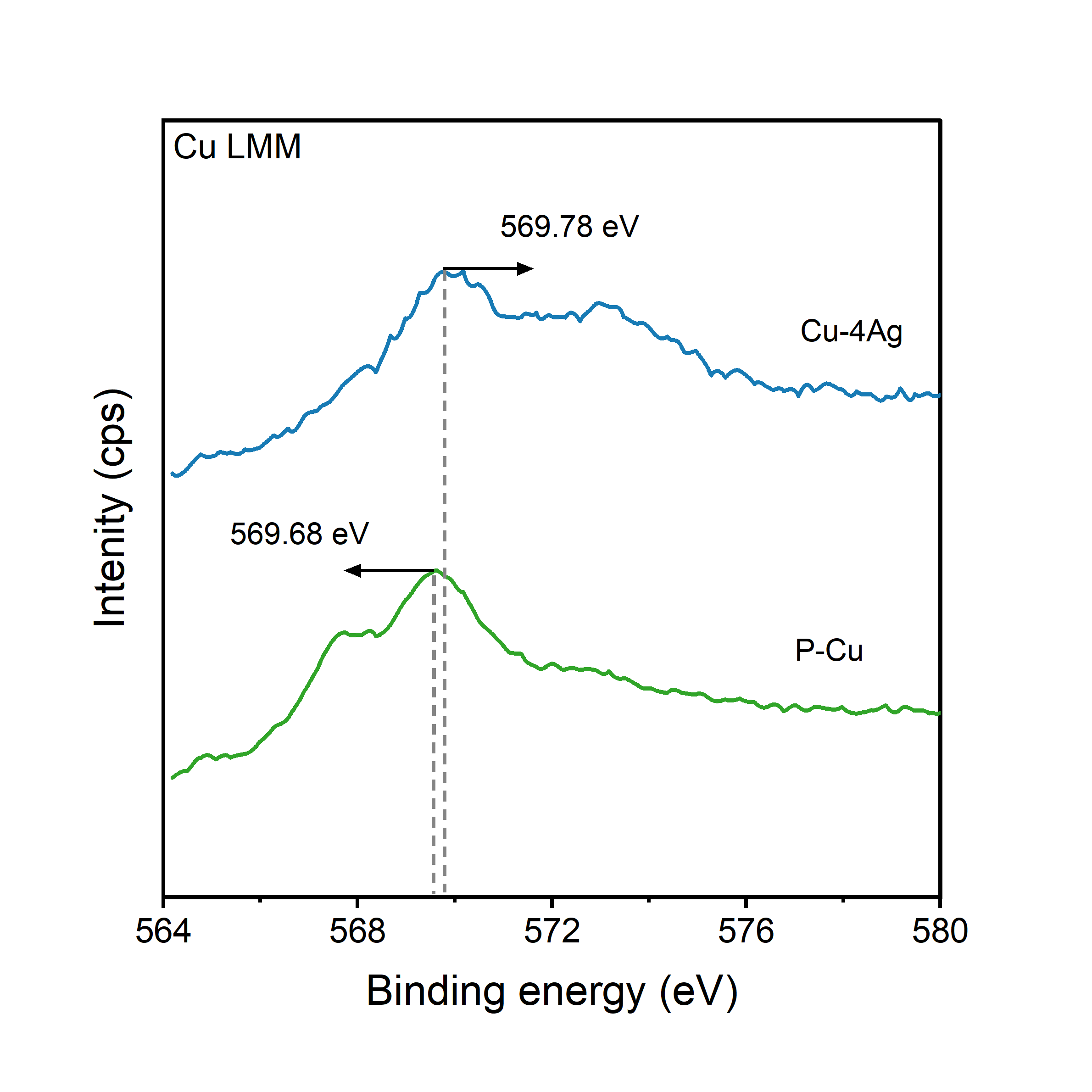
**Fig. S11.** (a) SEM image of Cu–4Ag after stability test. (b, c) EDS elemental mapping of Cu and Ag, respectively.



**Fig. S12.** XRD patterns of Cu–4Ag before and after stability test: (a) survey spectra and (b) the enlarged area around Cu (111) peak.



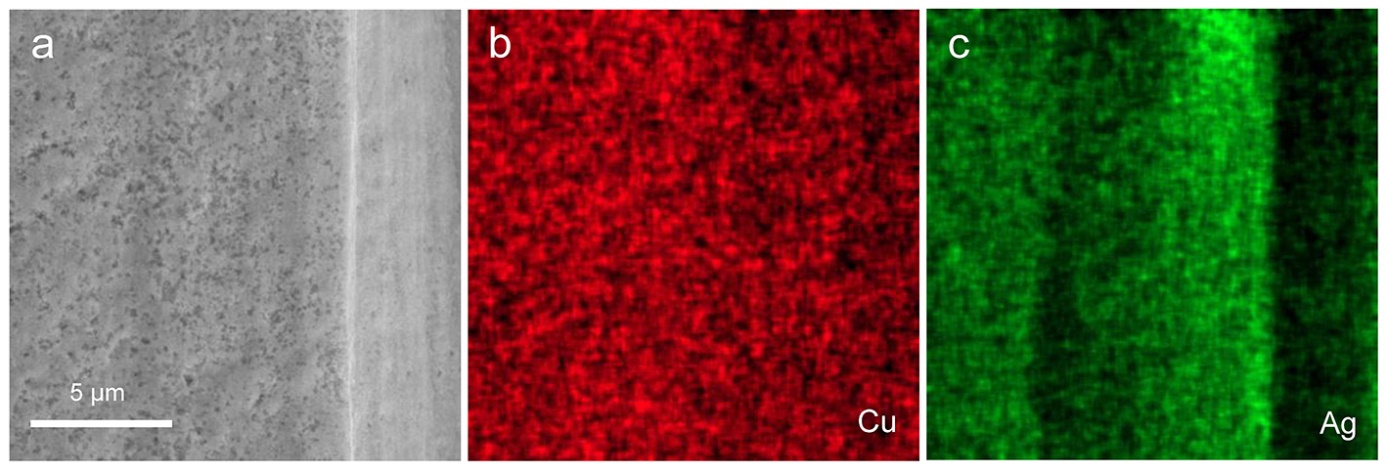
**Fig. S13.** HRTEM image of Cu–4Ag.



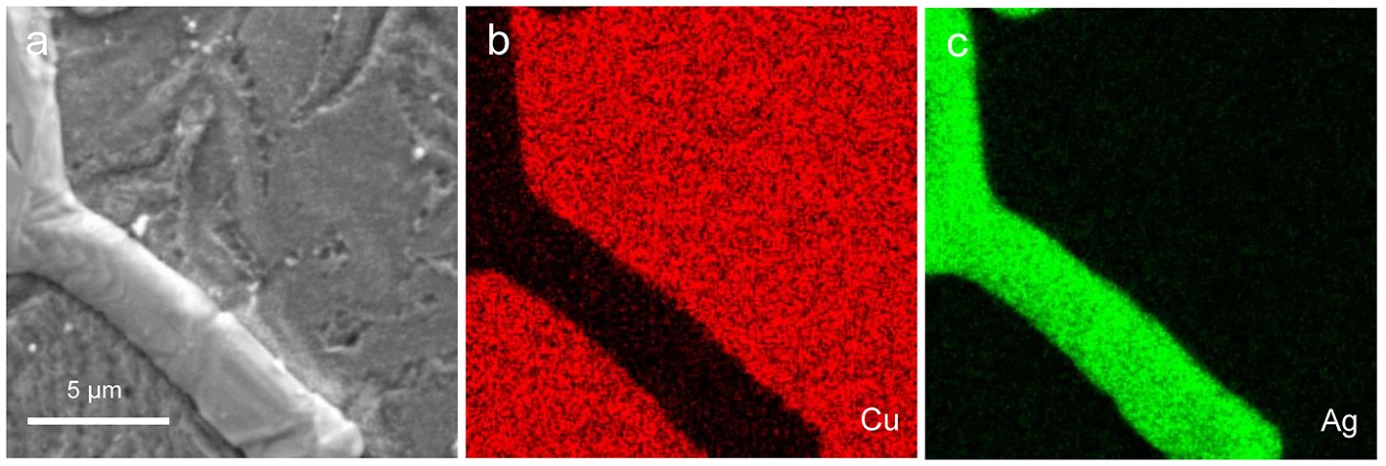
**Fig. S14.** Auger Cu LMM of P-Cu and Cu–4Ag.



**Fig. S15.** XPS of Cu–1Ag, Cu–4Ag, Cu plate, and Ag plate: (a) Cu 2p; (b) Cu 2p3/2; (c) Ag 3d; (d) Ag 3d5/2.



**Fig. S16.** (a) SEM image of Cu–4Ag D. (b) and (c) are the EDS elemental mapping of Cu and Ag, respectively.



**Fig. S17.** (a) SEM image of Cu–4Ag A. (b) and (c) are the EDS elemental mapping of Cu and Ag, respectively.



**Fig. S18.** XRD patterns of Cu–4Ag and Cu–4Ag A: (a) survey spectra and (b) the enlarged area around Cu (111) peak.



**Fig. S19.** XRD patterns of Cu–4Ag and Cu–4Ag D: (a) survey spectra and (b) the enlarged area around Cu (111) peak.



**Fig. S20.** XPS of Cu–4Ag A, Cu–4Ag, Cu plate, and Ag plate: (a) Cu 2p; (b) Cu 2p3/2; (c) Ag 3d; (d) Ag 3d5/2.



**Fig. S21.** XPS of Cu–4Ag D, Cu–4Ag, Cu plate, and Ag plate: (a) Cu 2p; (b) Cu 2p3/2; (c) Ag 3d; (d) Ag 3d5/2.



**Fig. S22.** Comparison of Cu–4Ag and Cu–4Ag A: (a) LSV polarization curves and (b) Nyquist plots.



**Fig. S23.** Comparison of Cu–4Ag and Cu–4Ag D: (a) LSV polarization curves and (b) Nyquist plots.

**Table S1.** Summary on HER properties of CuAg electrocatalysts

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| Catalysts | Electrolyte | Overpotential at 10 mA/cm2 / mV | Ref. |
| Cu–4Ag | 0.5 M H2SO4 | 256 | This work |
| Cu–3Ag | 0.5 M H2SO4 | 295 | This work |
| Cu–2Ag | 0.5 M H2SO4 | 318 | This work |
| Cu–1Ag | 0.5 M H2SO4 | 339 | This work |
| Cu3Ag1 | 0.5 M H2SO4 | 412 | [1] |
| Ag/Cu-CPE | 0.5 M H2SO4 | ~550 | [2] |

References

1. T.T. Yang, C.Q. Cheng, L.Y. Xiao, et al., A descriptor of IB alloy catalysts for hydrogen evolution reaction, SmartMat, (2023), art. No. e1204. <https://doi.org/10.1002/smm2.1204>
2. N. Behrooz, A. Ghaffarinejad, and N. Sadeghi, Ag/Cu nano alloy as an electrocatalyst for hydrogen production, *J. Electroanal. Chem.*, 782(2016), p. 1.