<div align="center">

Supporting Information

For

Ag-doped Cu Nanosheet Arrays for Efficient Hydrogen Evolution Reaction

</div>

Ling-Jie Kong‡, Ya-Meng Xie‡, Xing-Yu Chen‡, Cong Xi, Fei-Fei Zhang, Min Wang, Long Shang,, Yuan Huang*, Xi-Wen Du*, Sergei A. Kulinich*

Institute of New-Energy Materials, School of Materials Science and Engineering, Tianjin University, Tianjin 300072 (China)
E-mail: skulinich@tokai-u.jp; xwdu@tju.edu.cn; yi_huangyuan@tju.edu.cn

1. Experimental Section

Cutting and cleaning of copper foil and zinc foil: Firstly, the copper foil was cut to 1 cm × 1.5 cm, and the size of zinc foil was 1.2 cm × 1.8 cm. The copper foil was put in 0.5 M H_2SO_4 and distilled water for 40 min to remove surface oil and oxide. The cut zinc foil was placed in distilled water for 30 min, after which it was cleaned with deionized water and dried with a blower.

Sample preparation: Cu-Ag samples were prepared by high temperature sherardizing and acid etching. Firstly, the copper foil (1 cm × 1.5 cm), after ultrasonic cleaning, was immersed in $AgNO_3$ solution (0.75 g L^{-1}) for 30 s and dried naturally. The second step was to clamp the replaced copper foil with silver between two layers of zinc foil (1.2 cm × 1.8 cm each) and pressed at 25 MPa for 1 h to make the silver particles contact with the copper foil more closely. Then, the sample was placed in a tube furnace, and the temperature (at rate of 10 °C min^{-1}) was increased to 700 °C and kept for 6 h. After the holding time, the sample was rapidly quenched to room temperature. Finally, after the furnace is completely cooled to room temperature, after which the sample was etched for 24 h in 20 mL of 0.5 M H_2SO_4. The catalyst was obtained after cleaning with deionized water and ethanol. In order to prevent the oxidation of the sample, the cleaned sample was dried in a vacuum drying oven at 60 °C. The thickness of copper foil and zinc foil in this paper is 0.1 mm and 0.3 mm respectively.

Preparation of control samples: To investigate the influence of different proportions of silver, copper and zinc on the formation and catalytic performance of samples, copper foil was immersed in $AgNO_3$ solutions with different concentrations (0 g L^{-1}, 0.37 g L^{-1}, 0.75 g L^{-1}, 1.5 g L^{-1}, 2.25 g L^{-1}, 3 g L^{-1}), and the following steps were the same. In order to investigate the influence of acid etching parameters, the samples were synthesized in the first three steps and then washed and dried in 0.5M H_2SO_4 solution for 8, 16 and 24 h.

2. Electrochemical Measurements

The three-electrode system was used in the electrochemical test: the bulk catalyst material was used as working electrode, saturated calomel electrode and carbon rod were used as reference electrode and counter electrode respectively, and the electrolyte was 1 M KOH (pH = 14). Before electrochemical test, the electrolyte was filled with N_2 for 30 min, and HER test was carried out after saturation. All the potentials in this work are converted into reversible hydrogen electrode (RHE) by Nernst equation, as follows:

$$E \, (\, vs.\text{RHE} \,) = E \, (\, vs.\text{Hg} \, / \, \text{HgO}) + 0.2251 + 0.0591 \times \text{pH}$$

In the aspect of electrode preparation, self-supporting electrode was used in this experiment. In order to ensure the accuracy of the test, the samples used for the test were cut into 0.5 cm × 1 cm rectangle and marked at 0.5 cm × 0.5 cm. The electrode area involved in the reaction was determined to be 0.25 cm^2. The contrast samples used were commercial Pt / C (20%) and 50 nm silver powder. The preparation of catalyst ink was as follows: 5 mg of catalyst and 5 mg of carbon black were weighed, 1 mL water and 25 μL Nafion were added, ultrasonic dispersion was carried out for 20 min, 6 μL of ink was dropped on polished glassy carbon electrode (loading capacity was 0.4 mg cm^{-2}), and natural drying was used for standby.

In the cyclic voltammetry curve (CV) test, the voltage range was from - 1 to - 0.2 V $vs.$ SCE, the scanning rate is 50 mV s^{-1}, and the number of scanning cycles was 30 – 50 until the curves coincided. Linear

sweep voltammetry (LSV) was used to measure the voltage range from - 1 to - 0.2V *vs.* SCE electrode, and the scanning rate was 5 mV s^{-1}. The measured curves need to compare the overpotential at the current density of 10 mA cm^{-2}, and the Tafel curve can be obtained from the polarization curve. The frequency range of EIS was 0.1 – 10^6 Hz. When testing the i-t curve, select the voltage at 10 mA cm^{-2} of the sample, set the scanning time for 50 h, after the stability test, continue to use the sample to repeat the polarization curve, and compare the overpotential at 10 mA cm^{-2} before and after the stability test to judge the stability of the catalyst. In order to test the stability of the sample under high current, the over potential of 400 mV was selected for 10 h. In this experiment, the voltage range was 0.47 – 0.52 V *vs.* RHE, and the scanning rate was 20 mV s^{-1} – 120 mV s^{-1}. The electrochemically active specific surface area (ECSA) of the catalytic material can be obtained by dividing the capacitance of the electric double layer by the capacitance of the ideal smooth copper surface (40 μF cm^{-2}).

3. Material Characterization

The as-prepared materials were examined using X-ray diffraction (XRD, Bruker-D8 advanced diffractometer with Cu Kα radiation), scanning electron microscopy (SEM, Hitachi S-4800), transmission electron microscopy (TEM, JEOL-2100F system equipped with EDAX Genesis XM2). For the preparation of TEM samples, the products were ultrasonically dispersed in ethanol, and the solution was dropped on a Mo grid coated with a holey carbon film and dried with air. In order not to destroy the nanosheets, samples were also scraped directly to the Mo grid. STEM images were performed using a JEOL ARM200F microscope with STEM aberration corrector operated at 200 kV. The convergent semi-angle and collection angle were 21.5 and 200 mrad, respectively. The aberration coefficient used was equal to 1 μm. Atomic force microscopy (AFM) analysis was performed in air with a Multimode 8 Nanoscope (Veeco). X-ray photoelectron spectroscopy (XPS) analysis was collected on a k-alpha ThermoFisher spectrometer (ThermoFisher Scientific).

4. Computational Details

The DFT calculations were carried out on Cu (111) and CuAg (111) surface to explore the influence of Ag doping with Cu on HER properties in alkaline environment by the Vienna Ab initio Simulation Package (VASP)[1,2] The nuclei–electron interactions were described by the projector augmented wave (PAW) potentials.[3] The generalized gradient approximation (GGA)[4] with the Perdew–Burke–Ernzerhof (PBE)[5] functional was used to represent the electron exchange–correlation interactions. Grimme's DFT-D3 correction method was used to account for the van der Waals (vdW) effects. [6] The wave functions of valence electrons were expanded by plane wave basis set with a cut off energy of 500 eV. 10^{-5} eV and 0.03 eV Å^{-1} were set respectively for the convergence criteria for energy and force during geometrical optimization. The vacuum space of 15 Å was applied to avoid the interactions along the z-direction and the Brillouin zone was sampled by a 3 x 3 x 1 Monkhorst–Pack mesh grid.[7] The doping metal surface was built with 4-layer 4 x 4 Cu (111) surface with one Cu atom replaced by Ag atom, making a doping ratio 1.56%. The strain was applied by stretching 8.5% of the lattice length of Cu bulk in three directions. The bottom two layers was fixed and the top two layers were allowed to freely move to reach the optimized configuration. Throughout the calculation, for aqueous-based materials, we also used an implicit solvent model to consider the effects of solvent environment through a polarized continuum model as implemented in VASPsol with the dielectric constant set to 78.4.[8] The climbing image nudged elastic band (CINEB) method was used to explore the water dissociation and H$_2$ formation barrier.[9,10]

The adsorption energy (E^{ads}_X) of each intermediate X was calculated by the following equation:

$$E^{ads}_X = E_{*X} - E_* - E_X$$

where E_{*X}, E_* and E_X are energies of metal surface with intermediate, clean metal surface, and each intermediate.

The Gibbs free energy (G) of the adsorbed H was calculated by

$$G = E_{DFT} + \Delta E_{ZPE} - T\Delta S$$

where E_{DFT} is the total electronic energy obtained with DFT, ΔE_{ZPE} is the zero-point energy correction and $T\Delta S$ is the entropy difference of the system obtained through vibrational frequency analysis.
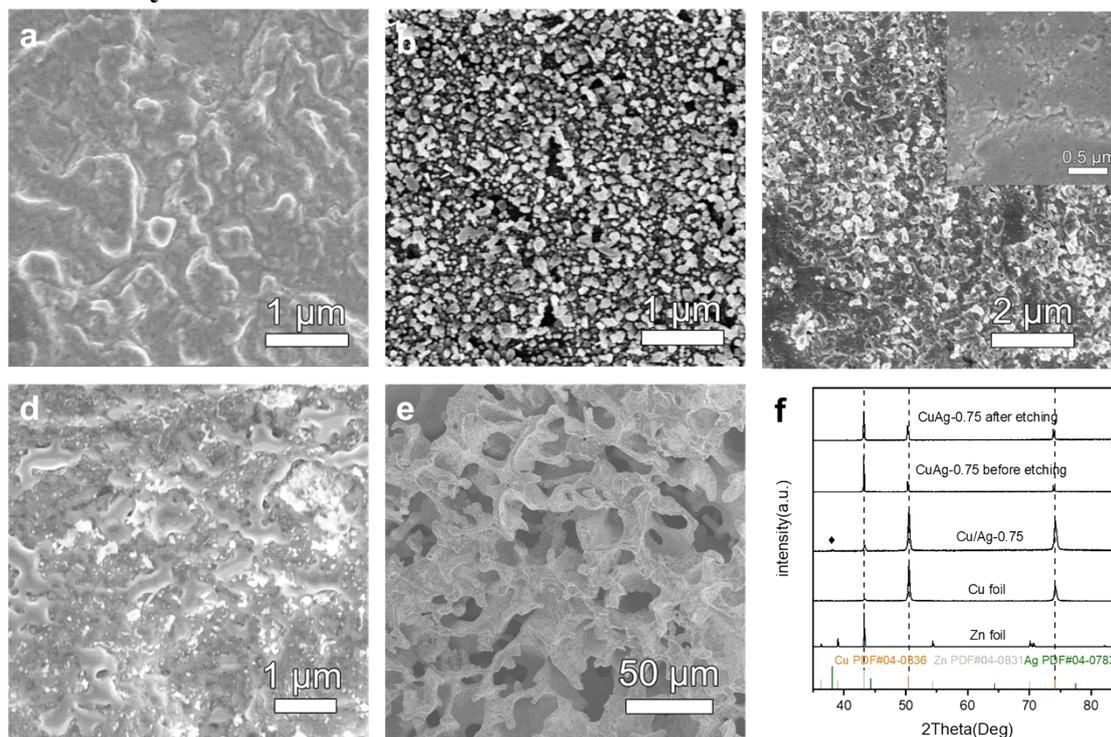
3. Supplementary Results

Fig.S1. SEM surface images of sample CuAg-0.75 at different stages of its preparation: (a) pure copper foil; (b) copper foil after galvanic replacement in aqueous $AgNO_3$ for 30 s; (c) copper foil coated with silver particles and compressed at 25 MPa; (d) copper foil kept between Zn foils at 700 °C for 6 h; (e) surface morphology of sample CuAg-0.75 after etching in 0.5 M H_2SO_4 for 24 h; (f) XRD patterns of the same sample at different preparation stages.
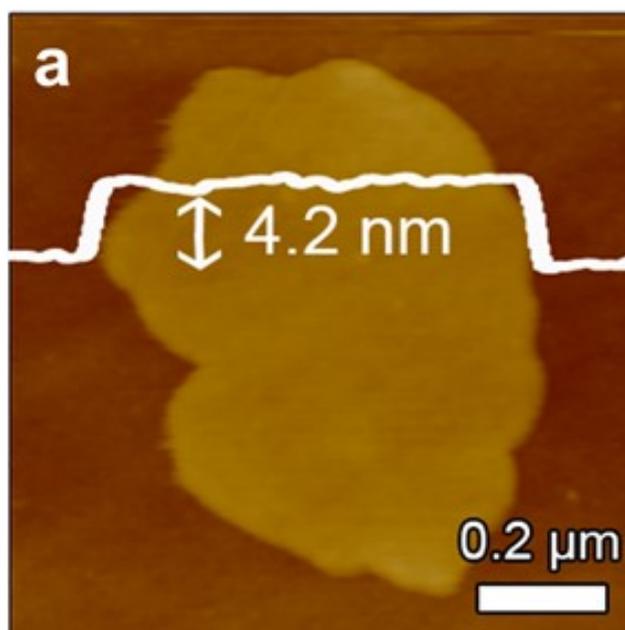
Fig. S2. AFM image of a sheet from sample CuAg-0.75.
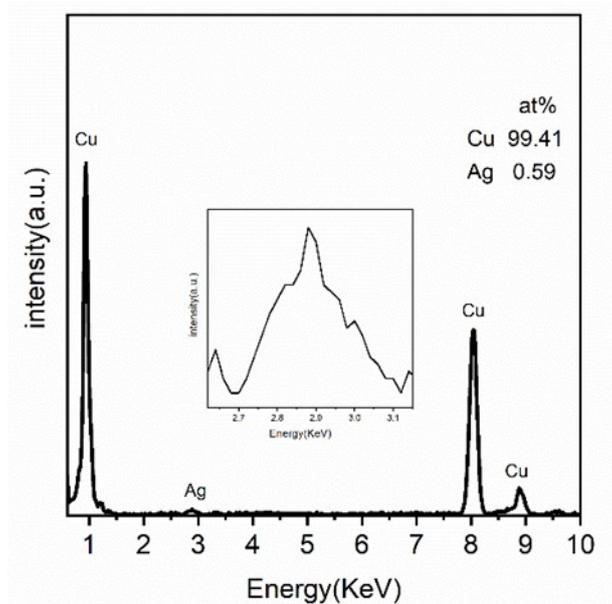
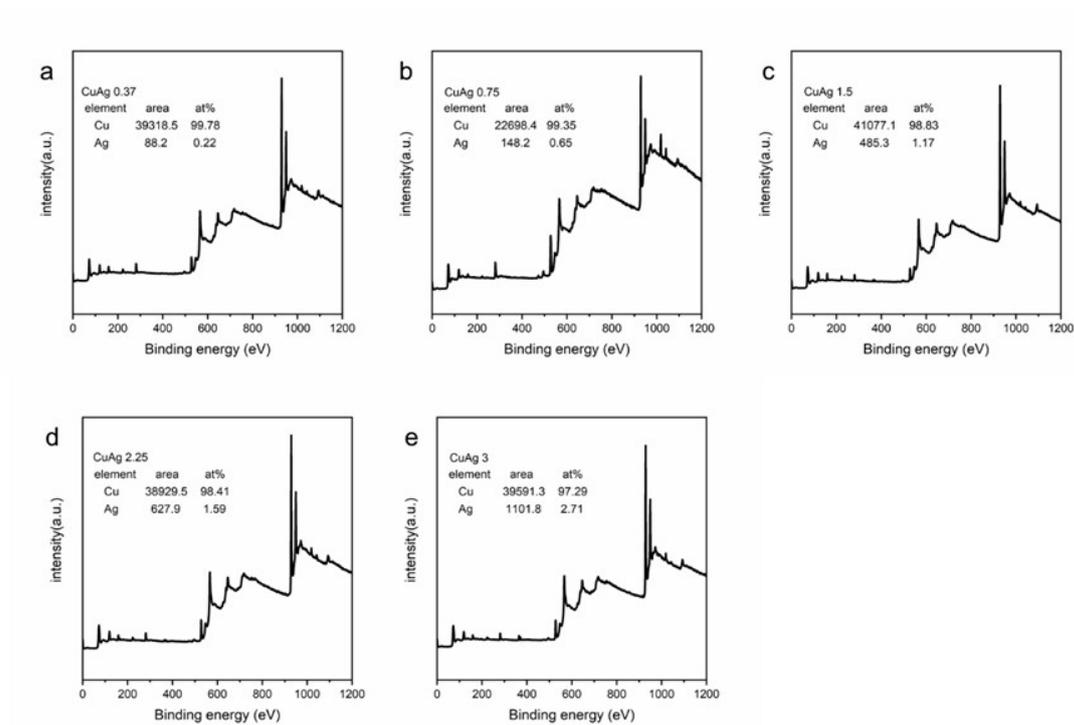**Fig. S3**. EDS spectrum of nanosheets from sample CuAg-0.75.

Fig. S4. XPS survey spectra of samples prepared at different silver ($AgNO_3$) concentrations. (a) 0.37 g L^{-1}; (b) 0.75 g L^{-1}; (c) 1.5 g L^{-1}; (d) 2.25 g L^{-1}; and (e) 3 g L^{-1}.
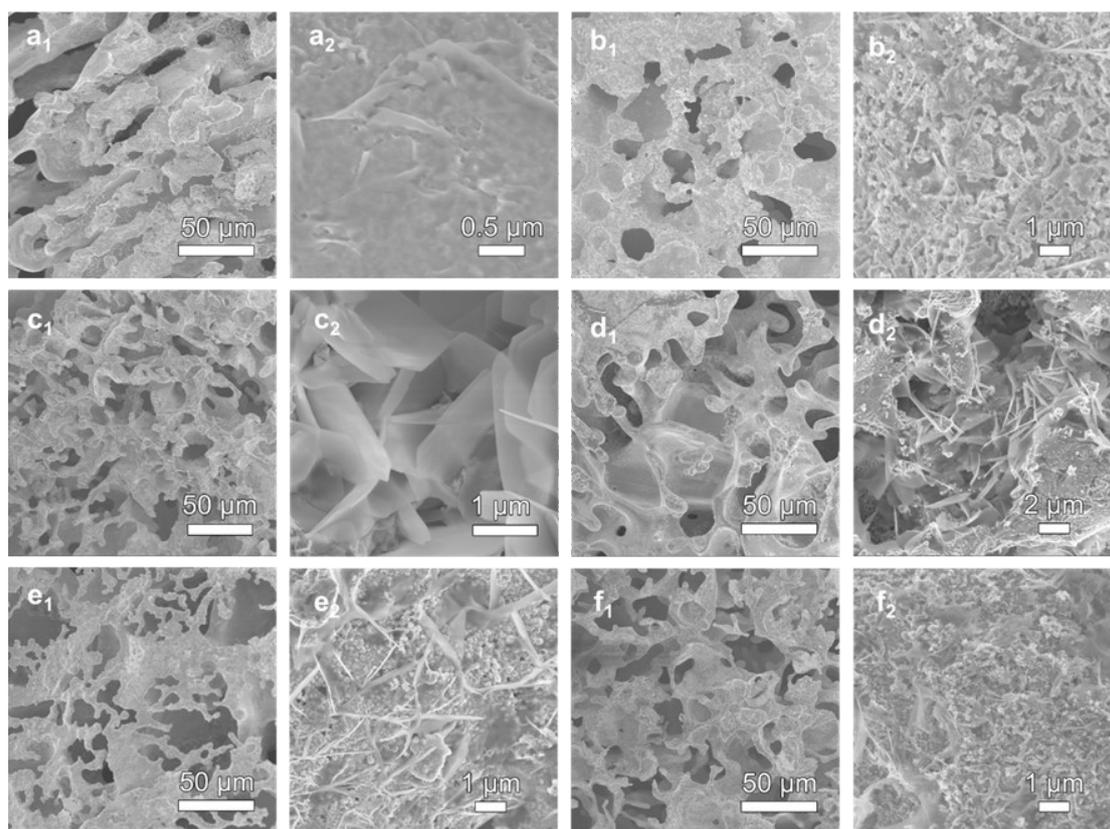
Fig. S5. SEM images of samples prepared at different silver ($AgNO_3$) concentrations. (a_1),(a_2) Without silver; (b_1),(b_2) 0.37 g L^{-1}; (c_1),(c_2) 0.75 g L^{-1}; (d_1),(d_2) 0.15 g L^{-1}; (e_1),(e_2) 2.25 g L^{-1}; (f_1),(f_2) 3.0 g L^{-1}
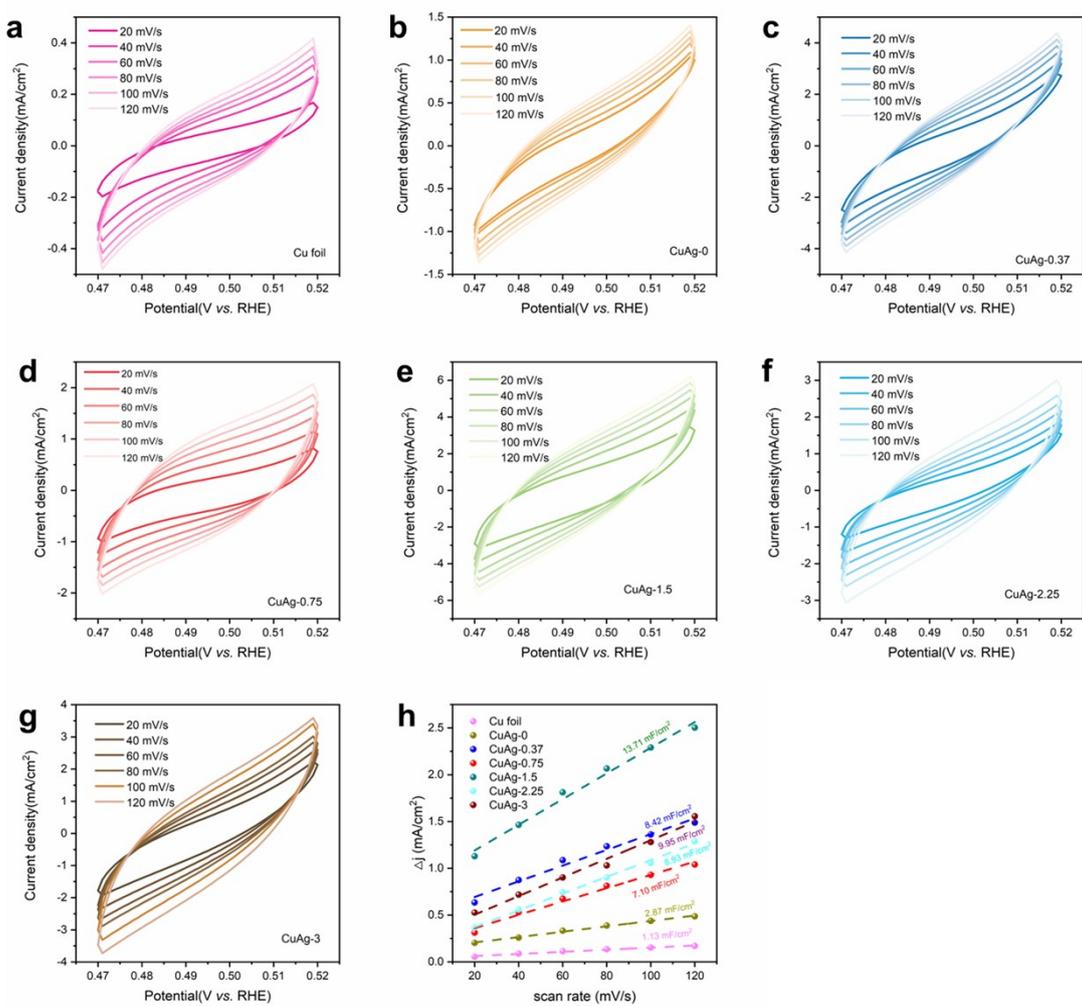
Fig. S6. Electrochemical active area of samples with different Ag content (samples CuAg-X). (a-g) CV curves of each sample at different scanning rates (20 mV s^{-1}-120 mV s^{-1}) in the range of 0.47-0.52 V $vs.$ RHE; (h) calculation of catalyst C_{dL}
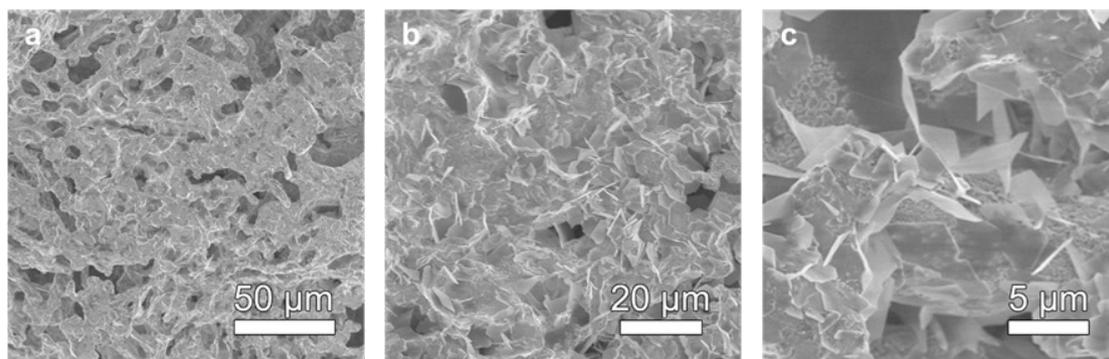
Fig. S7. SEM images of sample CuAg-0.75 subjected to 50-h-long stability test at current density of 10 mA cm^{-2}.
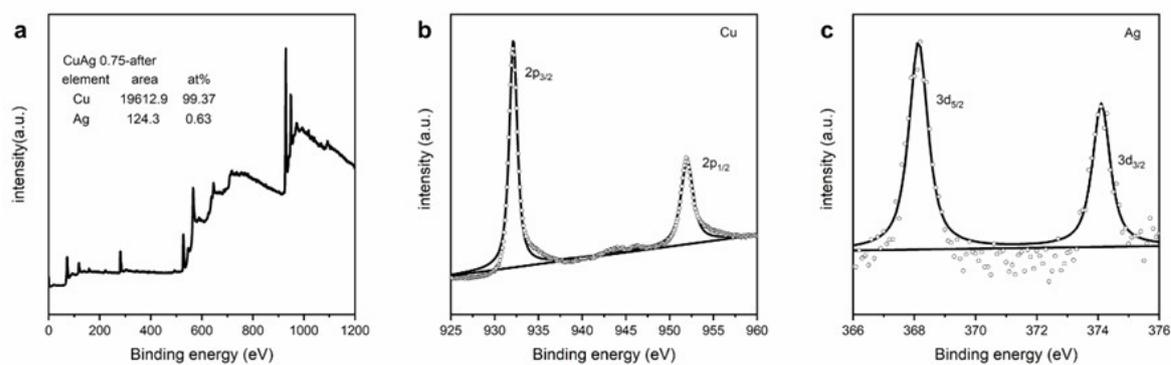

Fig. S8. XPS spectra of sample CuAg-0.75 subjected to 50-h-long stability test at current density of 10 mA cm^{-2}. (a) Survey scan; (b) Cu 2p spectrum; (c) Ag 3d scpectrum.
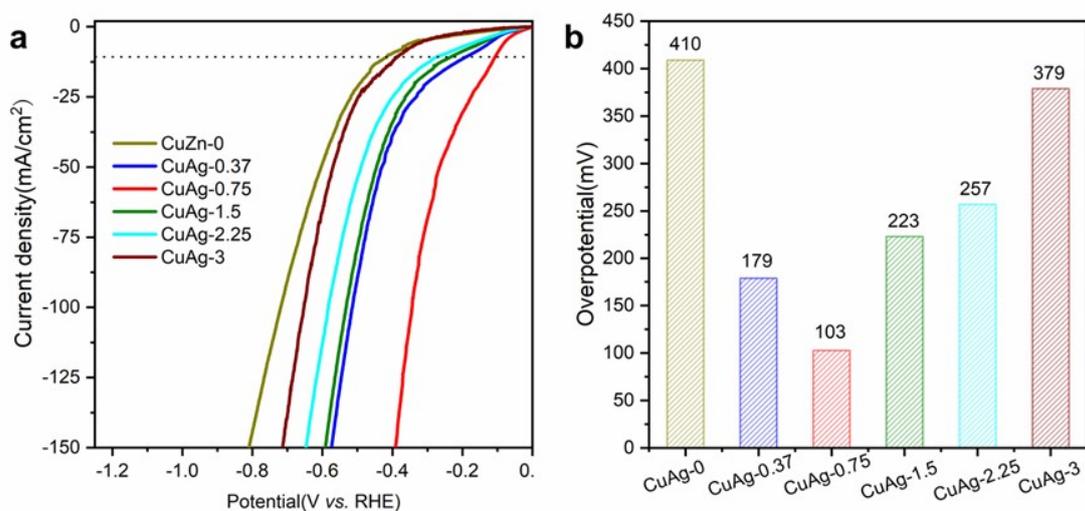
Fig. S9. Alkaline HER performance of samples prepared with different silver content (AgNO$_3$ concentration during galvanic replacement stage) on Cu foil before sherardizing. (a) Polarization curves and (b) overpotential at 10 mA cm^{-2} of samples CuAg-X with X=0, 0.37, 0.75, 1.5, 2.25 and 3.0 g L^{-1}.
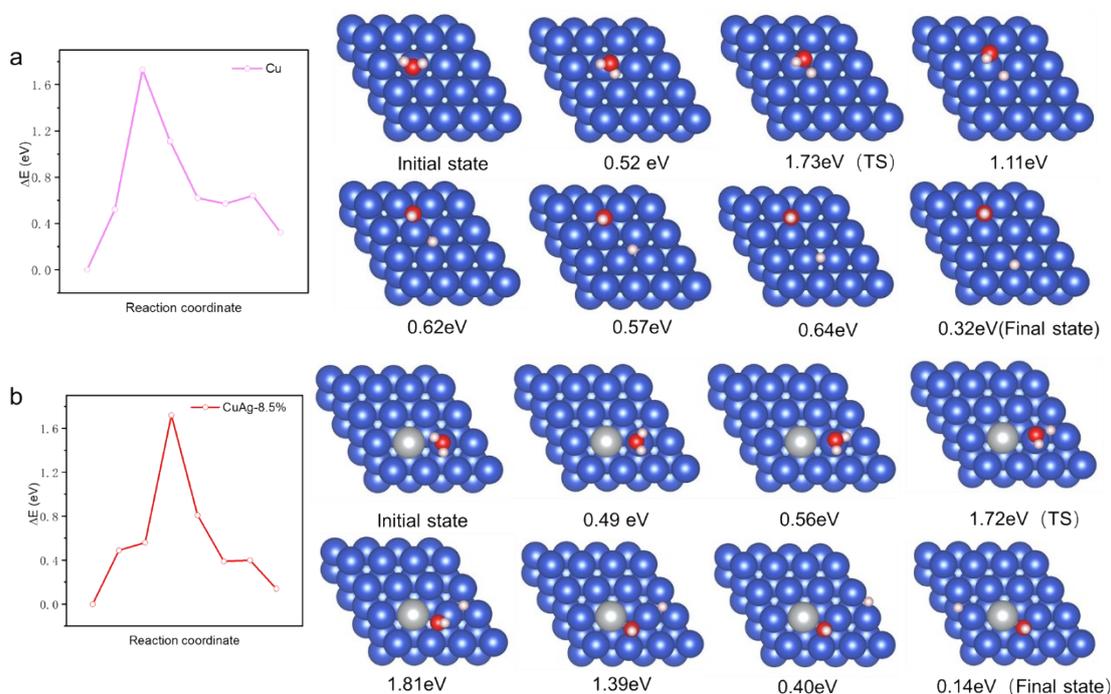
.

Fig. S10. Water dissociation barrier investigation for (a) pure Cu, (b) CuAg with 8.5% of tensile stress. Blue balls represent Cu atoms, and gray, red and white balls represent those of Ag, O and H, respectively.
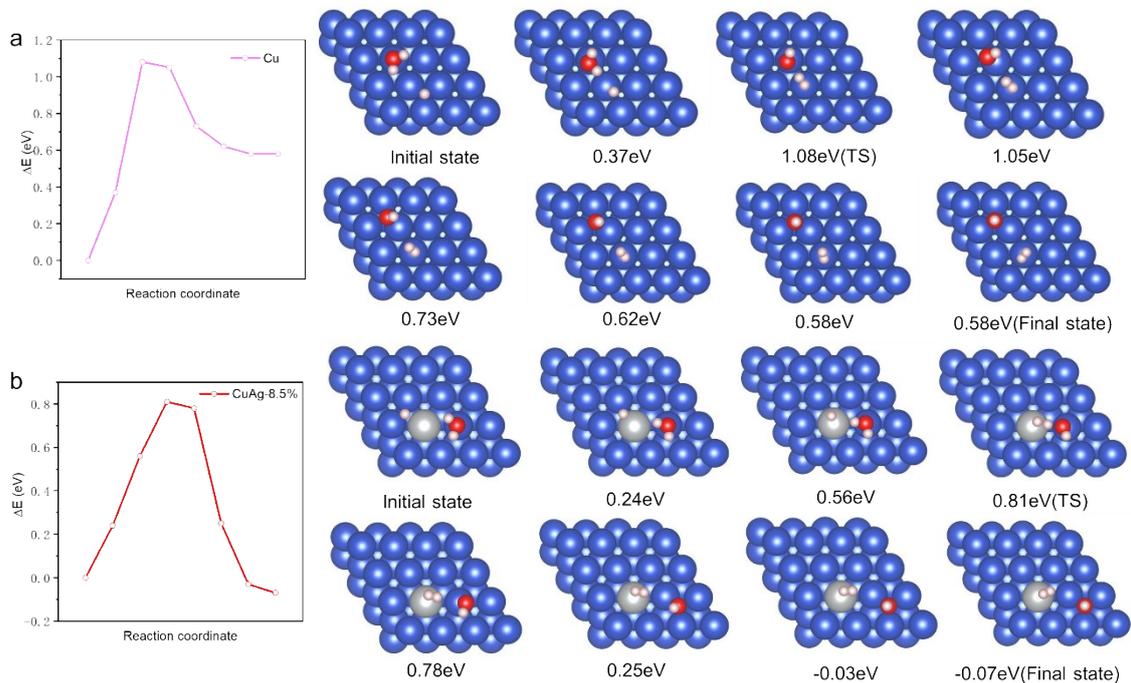
Fig. S11. H_2 formation and desorption barrier investigation for (a) pure Cu, (b) CuAg with 8.5% of tensile stress. The CuAg sample is seen to significantly decrease the H_2 formation barrier. Blue balls represent Cu atoms, and gray, red and white balls represent those of Ag, O and H, respectively.

Table S1. Water adsorption energies on different sites of pure Cu and CuAg with 8.5% tensile stress. Water adsorption on Cu atoms is constantly stronger than on of Ag atoms. Introduction of Ag atoms and resulting tensile stress enhance the adsorption strength on Cu atoms to water by 0.11 eV.

Species	Sites	HO-H(eV)
Cu	Cu (a)	0.32
CuAg-8.5%	Ag (e)	0.31
	Cu-1 (f)	0.17
	Cu-2 (g)	0.14

Table S2. Search for final states of water dissociation process on different sites of pure Cu and CuAg with 8.5% tensile stress, by moving the broken H from H_2O as the input structure of optimization. Cu-1 and Cu-2 indicate the first and second nearest Cu atoms to Ag, respectively. The tabulated energy is relative to the corresponding initio state energy of water adsorption. The introduction of Ag atoms and the resulting tensile stress are seen to enhance the dissociation strength

Species	Sites	H_2O (eV)
Cu	Cu	**-0.72**
CuAg-8.5%	Cu	**-0.83**
	Ag	-0.72

of Cu to water when the broken H falls onto a Cu atom in the vicinity of Ag.

Table S3. Hydrogen adsorption energy on different sites of pure Cu and CuAg with 8.5% tensile stress. The H adsorption active site is still Cu when Ag is doped. However, the introduction of Ag and the resulting tensile stress enhance the adsorption strength of Cu to H by 0.1 eV compared with pure Cu. Cu-1 and Cu-2 indicate the first and second nearest neighbor Cu atoms of Ag, respectively.

Species	Sites	H^*（eV）
Cu	Cu	0.41
CuAg-8.5%	Ag	0.63
	Cu-1	0.33
	Cu-2	0.34

References：

1. G. Kresse and J. Furthmuller, *Comput.* Mater. Sci., 1996, **6**, 15–50.

2. G. Kresse and J. Furthmuller, *Phys. Rev. B: Condens. Matter Mater. Phys*., 1996, **54**, 11169–11186.

3. P. E. Blochl, *Phys. Rev. B: Condens. Matter Mater. Phys*., 1994, **50**, 17953–17979.

4. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett*., 1996, **77**, 3865–3868.

5. J. P. Perdew, M. Ernzerhofand K. Burke, *J. Chem. Phys*., 1996, **105**, 9982–9985.

6. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys*., 2010, **132**, 154104–154123.

7. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B: Condens. Matter Mater. Phys*., 1976, **13**, 5188–5192.

8. K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T. A. Arias and R. G. Hennig, *J. Chem. Phys*., 2014, **140**, 084106–084114.

9. G. Henkelman, B. P. Uberuaga and H. Jonsson, *J. Chem. Phys*., 2000, **113**, 9901–9904.

10. G. Henkelman, A. Arnaldsson and H. Jonsson, *Comput. Mater. Sci*., 2006, **36**, 354–360