

Supporting information

Passivation of Cu nanosheets dissolution with Cu²⁺-containing electrolyte for selective electroreduction of CO₂ to CH₄

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Experimental section

Materials: Copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and Potassium bicarbonate (KHCO_3) were purchased from Aladdin Ltd. (Shanghai, China). Sulfuric acid (H_2SO_4) was bought from Sinopharm Chemical Reagent Co., Ltd. Carbon paper was purchased from Suzhou Sinero Technology Co., Ltd. and cleaned by sequential sonication in dilute sulphuric acid, ultrapure water, and ethanol several times. All the chemicals in the experiments were analytical grade and used without further treatments. Deionized water was purified through a Millipore system.

Preparation of the Cu NSs (Copper single crystal nanosheets)

The carbon paper substrate was cleaned sequentially in ethanol and water, each for 20 min through sonication treatment. The electrolyte is 0.1 M KHCO_3 solution. 1 μL 0.5 M CuSO_4 was added to 60 mL electrolyte. Afterward, fill the configured electrolyte with carbon dioxide gas until saturated. During *in-situ* growth, five cycles were performed under cyclic voltammetry test conditions with a potential range of $-0.1 \sim -2.2$ V vs. Ag/AgCl and scanning speed of 0.1 V s^{-1} . Five cycles were performed under linear voltammetry test conditions with a potential range of $-0.1 \sim -1.6$ V vs. Ag/AgCl and a scanning speed of 10 mV s^{-1} . The prepared Cu NSs electrode can be directly used for testing.

Control experiment

Cu-1 test, the performance of the Cu NSs is tested directly in electrolyte without replacement, which completes the electrode preparation. **Cu-0 test**, the Cu NSs prepared by *in-situ* electrochemical deposition were transferred to a new 0.1 M KHCO_3 electrolyte without any CuSO_4 addition. **Cu-2 test**, under Cu-1 test condition, 1 μL of 0.5 M CuSO_4 solution are added to the electrolyte. **Cu-3 test**, under Cu-1 test condition, 2 μL of 0.5 M CuSO_4 solution are added to the electrolyte. **Cu-4 test**, under Cu-1 test condition, 3 μL of 0.5 M CuSO_4 solution are added to the electrolyte. **Cu-10 test**, under Cu-1 test condition, 9 μL of 0.5 M CuSO_4 solution are added to the electrolyte.

Characterization: Powder X-ray diffraction (XRD) patterns were acquired on a Bruker D8 Discover diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Scanning electron microscopy (SEM) measurements were made on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 10 keV. Transmission electron microscope (TEM) images were taken on a Tecnai G2 F20 electron microscopy (FEI, Tokyo, America) at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-alpha X-ray photoelectron spectrometer using Al as the exciting source.

Electrochemical measurement: All electrochemical properties of as-prepared electrodes were tested in KHCO₃(0.1 M)/CuSO₄ or KHCO₃ (0.1M) electrolyte in a three-electrode system. LSV measurements were obtained at a sweep rate of 5 mV s⁻¹. LSV for testing was performed in the potential range of -1 ~ -1.6 V vs. Ag/AgCl. All potentials mentioned in this work were calibrated to the RHE by the equation. $E(\text{RHE}) = E(\text{Ag}/\text{AgCl}) + E_0(\text{Ag}/\text{AgCl}) + 0.0591 \times \text{pH} \text{ (V)}$.

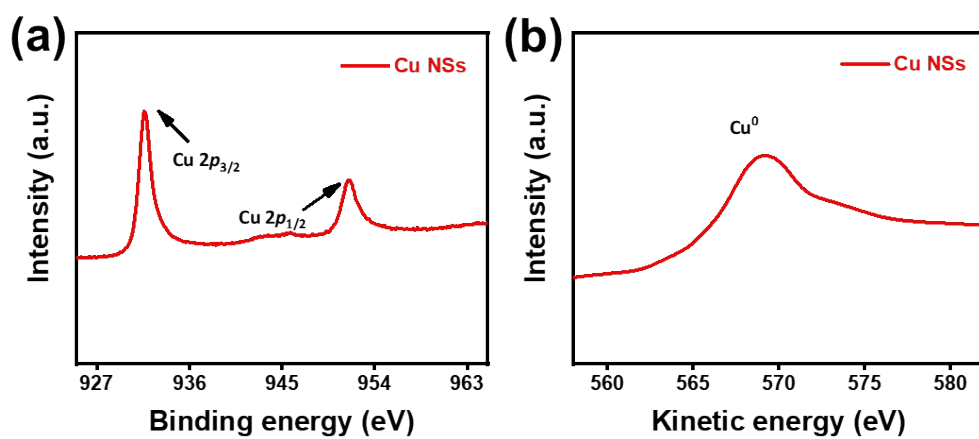


Fig. S1. The Cu 2p XPS spectra (a) and the auger electron spectrum of Cu LMM (b) of Cu NSs prepared by an *in-situ* electrochemical deposition method.

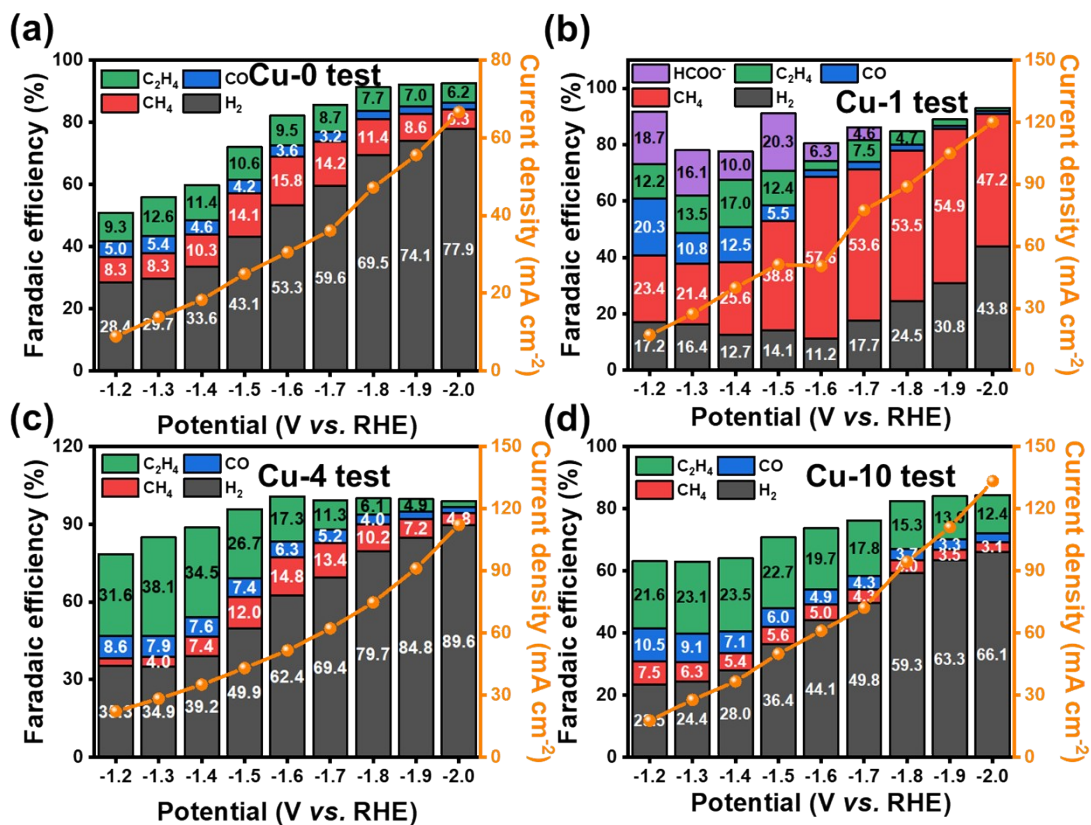


Fig. S2. The faradaic efficiency of Cu NSs under Cu-0 (a), Cu-1 (b), Cu-4 (c), and Cu-10 (d) test conditions after the electrochemical deposition for Cu NSs preparation in an H-type cell.

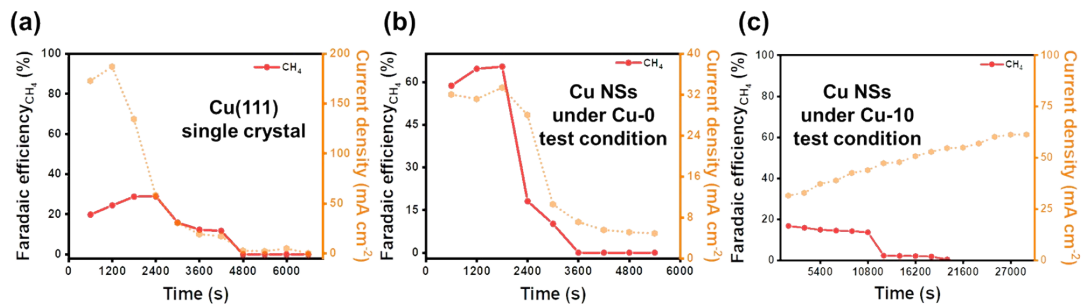


Fig. S3. The long-time faradaic efficiency stability tests of Cu(111) single crystal in 0.1 M KHCO₃ electrolyte (a) and Cu NSs under Cu-0 (b) and Cu-10 (c) test condition at -1.6 V vs. RHE.

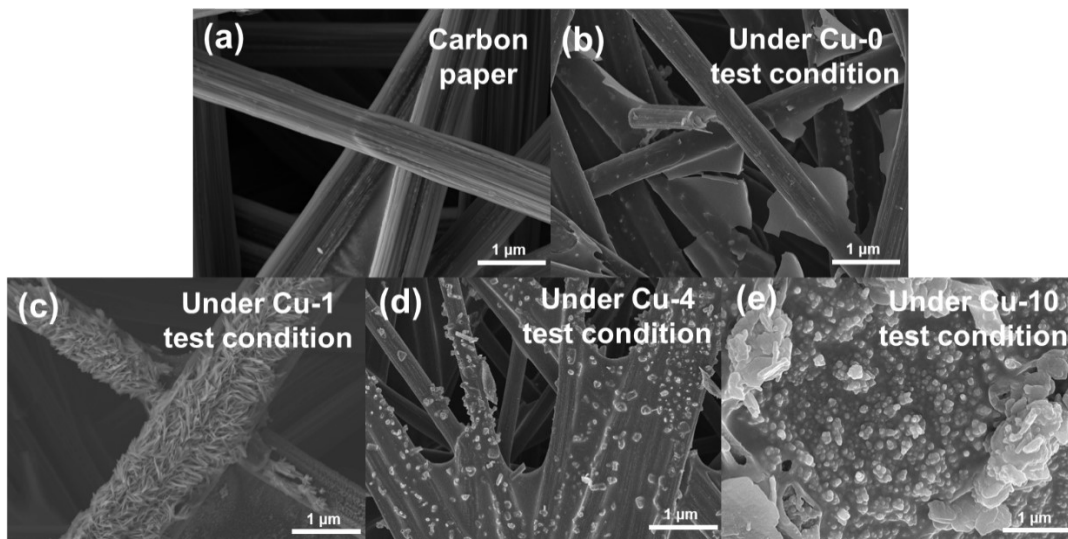


Fig. S4. The SEM images of the Carbon paper (a) and supported Cu catalysts after long-term performance test under Cu-0 (b), Cu-1 (c), Cu-4 (d), and Cu-10 (e) test conditions.

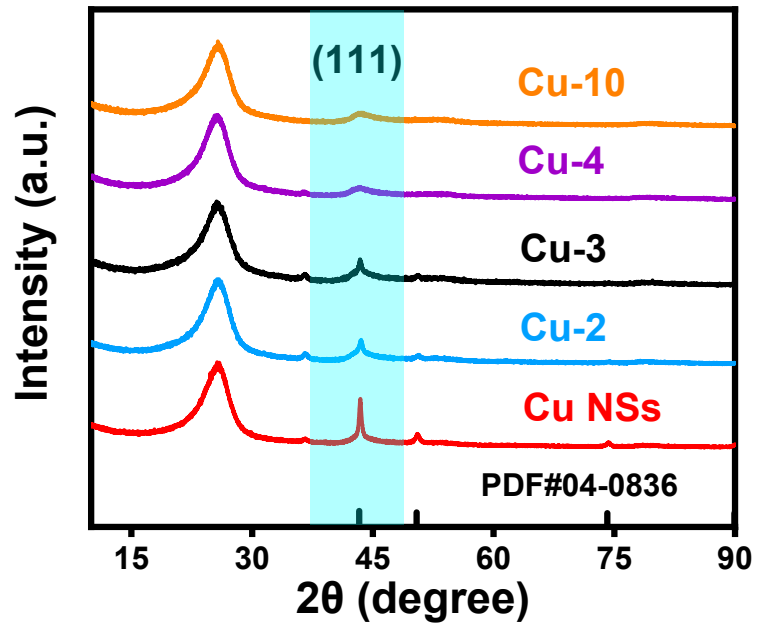


Fig. S5. The XRD patterns of Cu NSs in electrolytes with different Cu^{2+} content.

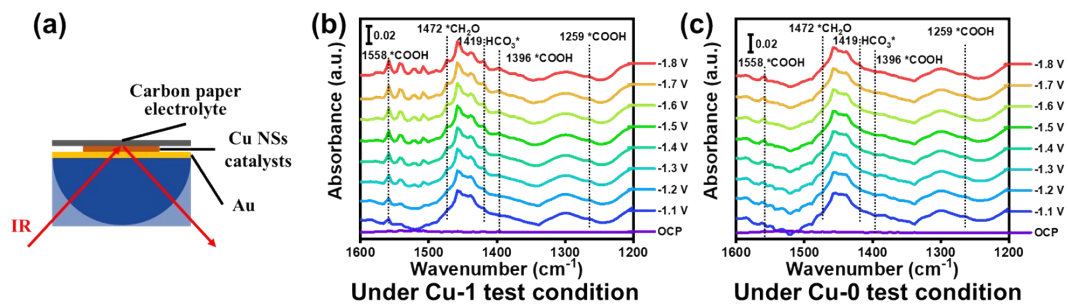


Fig. S6. (a) The test method of the *in-situ* FTIR experiments. The *in-situ* FTIR spectra of the Cu NSs under Cu-1 (b) and Cu-0 (c) test condition.

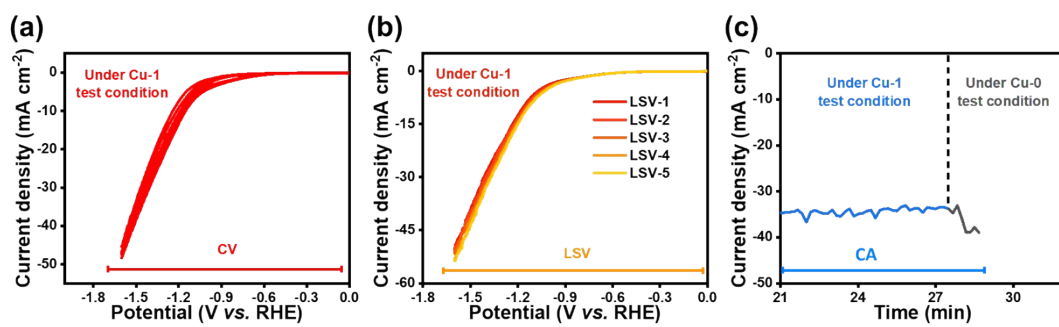


Fig. S7. The cyclic voltammetry (CV) curve, linear sweep voltammetry (LSV) curve and chronoamperometry (CA) curve during the *in-situ* EQCM-D tracking experiments.

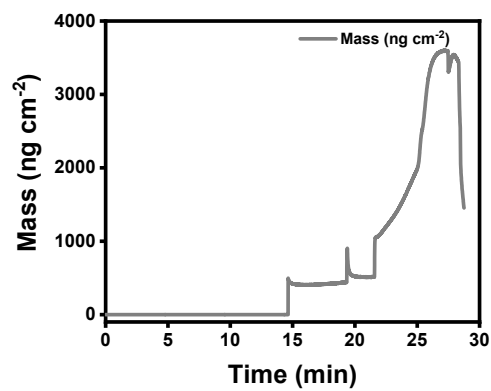


Fig. S8. The mass change under the condition of the chronoamperometry test after being transferred to Cu-0 test condition.