

Supporting Information

Graphdiyne/copper Sulfide Heterostructure for Active Conversion of CO₂ to Formic acid

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1. Electrochemical test method

Electrochemical measurements were performed using a typical three-electrode system, with a catalyst as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a graphite rod as the counter electrode. Electrochemical measurements were performed using a CHI 760E electrochemical workstation (Chenhua Instruments, China) in a sealed H-type electrochemical cell separated by a cation exchange membrane (Nafion 117). The experiments were performed in an H-type electrochemical cell containing 25 mL of 0.1 M KHCO₃ electrolyte on each side of the cell. The linear voltammetry sweep (LSV) measurement was carried out at room temperature with Ar and CO₂ atmospheres respectively. The scan rate was 5 mV s⁻¹. During all experiments, gaseous products at the cathode outlet were collected and detected by electrochemical gas chromatography. Additionally, liquid products are quantified and analyzed by nuclear magnetic resonance (NMR). All potentials reported in this work are referred to the reversible hydrogen potential (RHE).

According to: $E_{\text{RHE}} = E_{\text{SCE}} + E_{0(\text{SCE})} + 0.059\text{pH}$,

Convert the measured potential to the reversible hydrogen potential (RHE).

Liquid products were analyzed on a NMR instrument Varian WM-400 (400 MHz). After 2 h of CO₂ reduction reaction, withdraw 5 ml of electrolyte (0.1 M KHCO₃ aqueous solution) from the cathode compartment of the electrochemical reactor via syringe and mix it with 10 μl of chromatography-grade dimethyl sulfoxide sonicated. Take 0.5 ml of the mixture and mix with 0.1 ml DO (99.9%), finally transfer to an NMR sample tube and calculate the liquid product concentration with reference to the internal standard (dimethyl sulfoxide).

The in-situ attenuated total reflectance Fourier transform infrared (ATR-FTIR) measurements were conducted in a single chamber electrochemical cell containing CO₂-saturated 0.1 M KHCO₃ aqueous electrolytes. A Bruker VERTEX 70v Fourier Transform Infrared Spectrometer (FTIR) equipped with a N₂-cooled MCT detector was employed for the measurements. CO₂-saturated 0.1 M KHCO₃ aqueous solutions were used as the electrolytes. The spectra were recorded at the resolution of 4 cm⁻¹ with 32 scans. Potential-resolved in-situ ATR-FTIR spectra were collected in CO₂-saturated 0.1 M KHCO₃ electrolyte at different potentials. All (spectro)-electrochemical experiments were conducted at room temperatures.

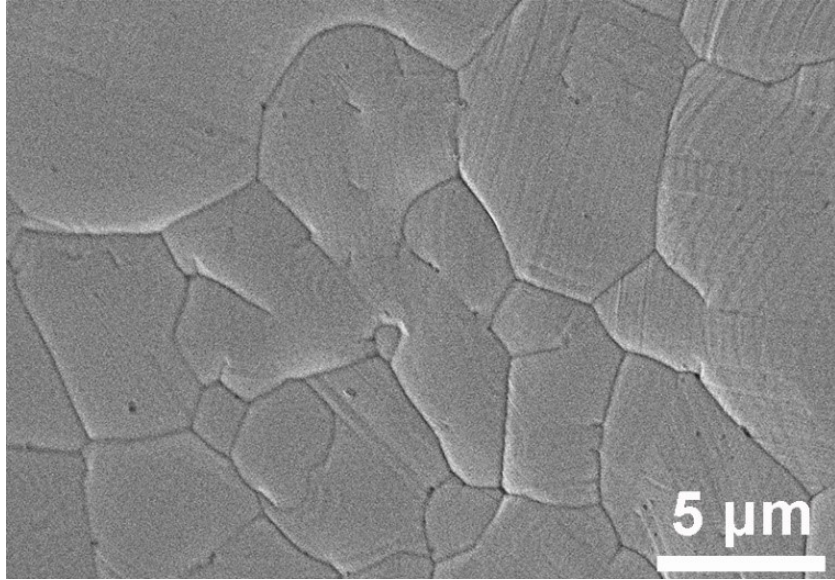


Fig. S1 SEM image of Cu foam

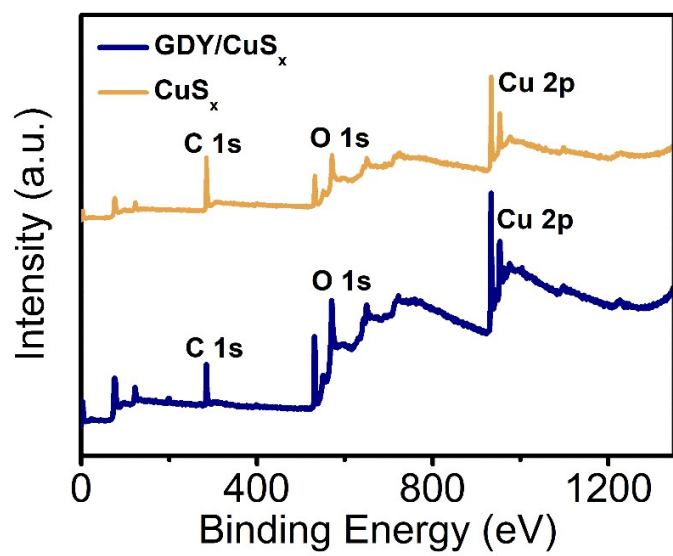


Fig. S2 XPS survey spectra of CuS_x electrode and GDY/CuS_x electrode

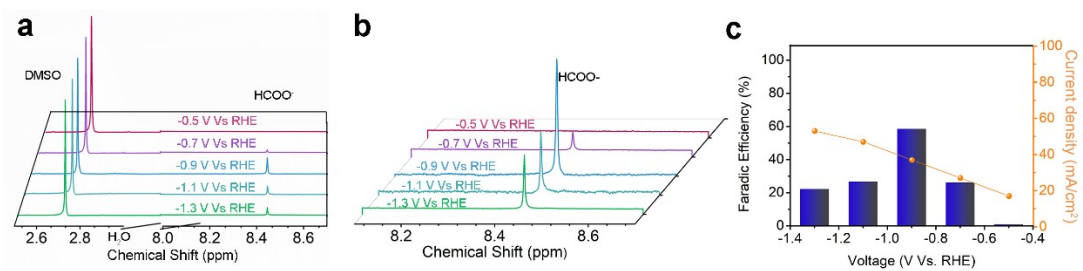


Fig. S3 a, b) ¹H NMR spectra the of CuS_x electrode electrolyte after CO₂RR at different applied potentials. c) Plot of FE and current density of CuS_x electrode

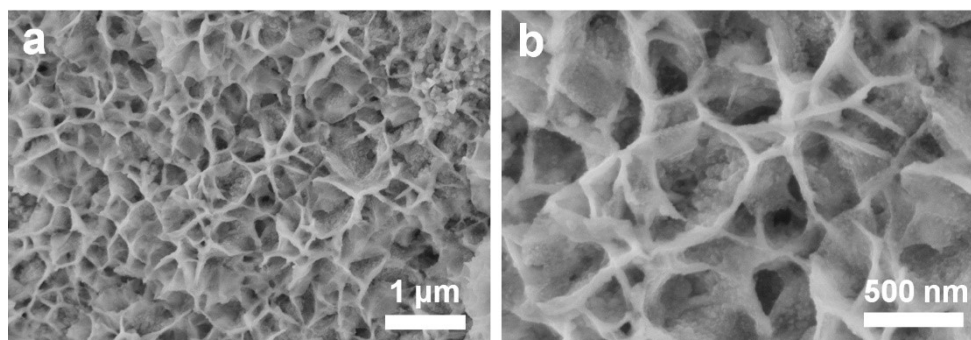


Fig. S4 (a) low- and (b) high-magnification SEM images of CuS_x/GDY obtained after the electrocatalytic tests.