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Electronic Supplementary Information

Electrochemical reduction of carbon dioxide to C2 products using a copper-sulfide, nanoparticle electrode synthesized by thermal decomposition of sulfur and copper-amine complex ink

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Experimental Section

Preparation of inks: Copper(II) formate anhydrate (Cuf) was used as the copper source, and was obtained by drying copper(II) formate tetrahydrate (> 98%, Kanto Chemical Co., Inc.) in a vacuum at 100 °C for 2 h. Octylamine (OA, > 98%, Kanto Chemical Co., Inc.) was used as a complexing agent. Sulfur powder (S, > 98%, FUJIFILM Wako Pure Chemical Corp.) was used as a sulfur source. Cuf and OA were mixed and vigorously kneaded for 2 min (Cuf-OA ink). S was added and kneaded (Cuf-OA-S ink). The molar ratio of the Cuf-OA-S ink was set to 1:2:1 (= Cuf:OA:S). A sample of Cuf-OA ink (Cuf:OA = 1:2) was prepared for comparison.

Fabrication of electrodes: A copper plate (25 x 15 x 1 mm, > 99.99 %, Nilaco Corp.) served as the substrate for the electrode. A coated area of the substrate (10 x 10 mm) was created using masking tape with a thickness of 50 μ m. The prepared ink was dropped onto the coated area, which was then spread via a squeegee method using the edge of a glass plate to form the ink film. The coated substrate was then placed into a bell jar type of oven (BV-001, Shibata Scientific Co., Ltd.), which was followed by calcination under a flow of nitrogen at 4 L/min. After the temperature was raised from 20 to 180 °C for Cuf-OA-S ink and to 140 °C for Cuf-OA ink at a heating rate of 5 °C/min, the temperature was maintained for 30 min prior to cooling. After the masking tape was peeled off, the back and sides of the Cu substrate were covered with insulating tape to allow exposure of only the copper and copper sulfide film. Thus, each film is the only the active site toward the electrochemical reduction of CO₂. An electrical wire was then pushed through a hole in the copper plate.

Characterization of electrodes: The morphologies of the surfaces and cross-sections of the prepared films were observed using a Scanning Electron Microscope (SEM, VE-7800,

KEYENCE Corp.). Nanoparticle size and lattice spacing was investigated using a Transmission Electron Microscope (TEM, JEM-3000F, JEOL., Ltd.) equipped with an imaging filter (GIF-2000, Gatan., Inc.). The crystallite phase of the films was measured by X-ray diffractometer (XRD, RINT 2200V, Rigaku Corp.).

Electrochemical reduction of CO₂: Electrochemical reduction of CO₂ on the fabricated electrodes was conducted using a three-electrode method in a two-compartment H-type cell, which was separated by a cation exchange membrane (Nafion NRE-212, DuPont). We filled the cell with 30 mL of a 1 M KHCO₃ electrolyte solution (>99.5 %, FUJIFILM Wako Pure Chemical Corp.) at pH 8.0. The fabricated-film working electrode and the Ag/AgCl (saturated KCl solution) reference electrode were each immersed in the cathodic compartment. As the counter electrode, a Pt plate was immersed in the anodic compartment. The three electrodes were connected to a potentiostat (pocketSTAT, Ivium). CO₂ was continuously purged in the cathodic compartment at a flow rate of 30 mL/min. The potential was changed from -0.3 to -0.9 V vs. Ag/AgCl, and the current was measured after 20 min. The potential vs. Ag/AgCl was converted to the potential vs. RHE (reversible hydrogen electrode) at pH 8.0, based on the Nernst equation. Measured potential ranged from 0.37 to -0.23 V vs. RHE.

Analysis of product gasses: During the electrochemical reaction of CO_2 at each potential, 1 mL of produced gasses was extracted from the catalyst side of the H-type cell using a syringe. These gasses were injected to a gas chromatograph (GC-4000, GL Sciences Inc.) equipped with a flame ionization detector (FID, GL Sciences Inc.) and a metanizer (MT221, GL Sciences Inc.) to detect CO, CH₄, and C₂H₄. The data obtained from gas chromatography were treated using SIC 480II software (SYSTEM INSTRUMENTS Co., Ltd.). Calibration curves of each of the gasses produced were

prepared for quantitative analysis and the rates of production were calculated by dividing the volume fraction of produced gasses by the total gas volume fraction.