

Supplementary Information for

Structural identification of oxide-derived Cu electrocatalysts: A comparative study of electrochemical vs. thermal reduction of Cu oxide

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Methods and Materials

Preparation of OD-Cu catalysts.

OD-Cu-ER. First, a uniform layer of blue $\text{Cu}(\text{OH})_2$ nanowires was prepared by the chemical oxidation of Cu foam. Each Cu foam piece was initially washed with hydrochloric acid (36 %) for 1 min to remove its native oxide layer, followed immediately by sequential ultrasonic cleaning in acetone, ethanol, and deionized water for 5 min. The cleaned Cu foam was immersed in 100 mL of an aqueous solution containing 4.8 g of NaOH and 2.282 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ for 30 min at around 5 °C. The Cu foam was removed from the solution, thoroughly rinsed with ultrapure water, and dried to obtain blue $\text{Cu}(\text{OH})_2$ nanowires. The black CuO nanowires were then obtained after the Cu foam with a layer of $\text{Cu}(\text{OH})_2$ nanowires was annealed in air at a preset temperature of 180 °C for 1 h. Subsequently, the CuO nanowires on the Cu foam were then reduced at -2 mA cm^{-2} for 1800 s in CO_2 -saturated 0.1 M KHCO_3 aqueous electrolyte, resulting in OD-Cu-ER.

OD-Cu-HR. CuO electrodes were prepared at 180 °C as described above. Instead of electrolytic reduction of the CuO layer, electrodes were reduced under an H_2 atmosphere. Oxidized electrodes were placed in a tube furnace with flowing H_2 at 100 sccm and heated at 300 °C for 2 h.

SEM and TEM characterization.

Scanning electron microscope (SEM) measurements were performed at Thermo Scientific™ Apreo at acceleration voltage of 5kV. Transmission electron microscope (TEM) characterization were carried at Thermo Scientific™ Talos F200X. The Cu foam with different catalysts was dispersed in ethanol by sonification. The samples for TEM were prepared by dropping and drying the ethanol dispersions, on the carbon-coated molybdenum grid at room temperature.

In order to investigate the true surface of catalysts, we minimize the chance of direct exposure of the samples to air. The catalysts reduced by H_2 are preserved in Ar until the temperature drops to room temperature. The catalysts reduced or tested electrochemically are dried by N_2 . Then each catalyst is transferred into glovebox rapidly until subsequent characterization.

XRD characterization. XRD-patterns of the catalysts were collected using a Rigaku Smartlab9KW (RIKEN) equipped with a Cu K α ($\lambda = 0.15406$ nm) irradiation source. Samples were analyzed in a 2θ range of 20-80 $^\circ$ at a speed of 20 $^\circ$ /min.

XPS characterization. X-ray photo spectroscopy (XPS) measurements were carried out with ESCALAB 250Xi (Thermo Scientific) using a monochromatic Al K α X-ray beam (1486.6 eV). All binding energies were referenced to the C 1s peak (284.8 eV).

Electrochemical Measurements. Electrochemical measurements were performed at ambient temperature and pressure in a customized gastight H-type glass cell separated by a Nafion 117 membrane. Each chamber was filled with 30 ml of 0.1 M KHCO₃ solution. A piece of Pt foil (2 cm \times 2 cm \times 0.2 cm) was used as counter electrode and Ag/AgCl electrode as reference electrode (KCl sat.). The treated Cu foam (1 cm \times 1 cm) was served as work electrode. Before reaction, CO₂ was purged into electrolyte for 30 min to saturate the solution (pH = 6.8). The CHI 660e potentiostat was employed to perform the reduction of CO₂ and other electrochemical tests. During electrochemical reaction, the CO₂ was continuously purged at 30 sccm regulated by mass flow controller and controlled potential electrolysis was conducted to perform electrochemical reduction of CO₂. All reported potentials were calibrated to the RHE scale as follows: $V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.197 \text{ V} + 0.059 \times \text{pH} - i \times R_{\Omega}$. The Ohmic drop (R_{Ω}), determined by electrochemical impedance spectroscopy, was corrected automatically 85% by electrochemical workstation and the rest was corrected manually.

After the gas steam passed the cell, it was directly introduced into a Gas Chromatograph (GC, Shimadzu GC 2030) equipped with BID detector for products separation and analysis. The high purity He gas was used as carried gas for GC. The concentration of product gases was determined using calibration curves from standard gases.

The Faradaic efficiency can be calculated as follows

$$FE = \frac{z_i \times V_i \times V \times p \times F}{R \times T \times I}$$

Where z_i is the number of electrons transferred to produce a molecule; V_i is the measured volume concentration of product i ; V is the CO_2 flow rate (30 ml min^{-1}); p is the atmospheric pressure ($1.013 \times 10^5 \text{ Pa}$); F is the faradaic constant (96485 C mol^{-1}); R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$); T is the reaction temperature (298 K); I is the current measured by electrochemical workstation.

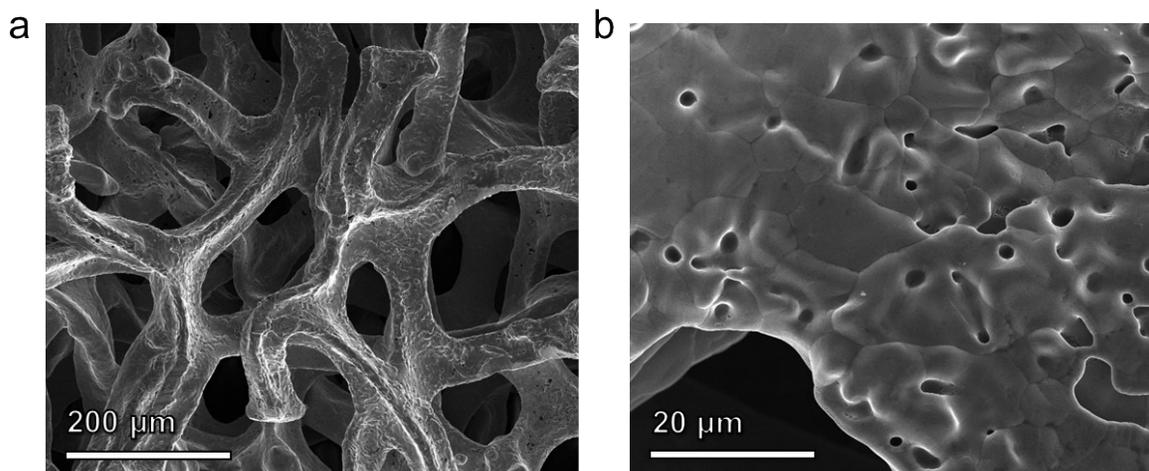


Figure S1 SEM image of starting material of Cu foam at different magnifications. Cu foam has the three-dimensional structure with different sizes of pores, ranging from tens of micrometers to a few micrometers. Therefore, Cu foam has larger surface area and can accommodate more catalysts, which results into higher current and reaction rate.

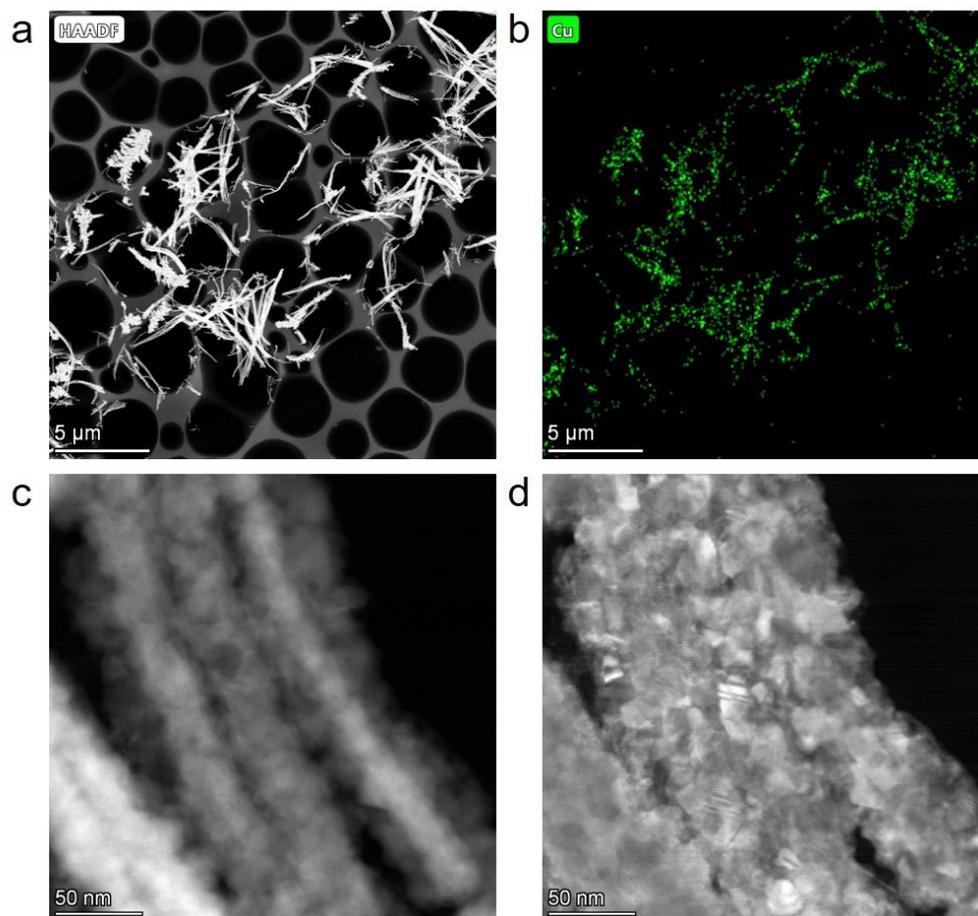


Figure S2. **a** and **b.** STEM image and corresponding EDS Cu map of CuO nanobelts scratched from the Cu foam. **c** and **d.** STEM images in HAADF (**c**) and DF (**d**) mode show the CuO nanobelts are composed of small particulates.

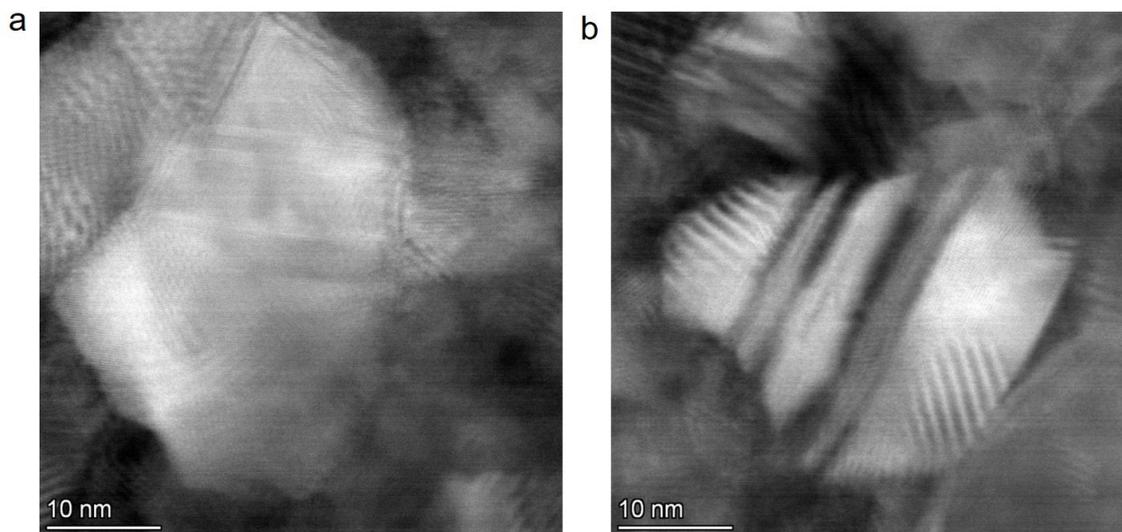


Figure S3. a and b. STEM images in DF mode illustrate the existence of rich defects structures e.g. stacking faults (a) and anti-phase boundaries (b) in a single Cu nanoparticle in CuO nanobelts.

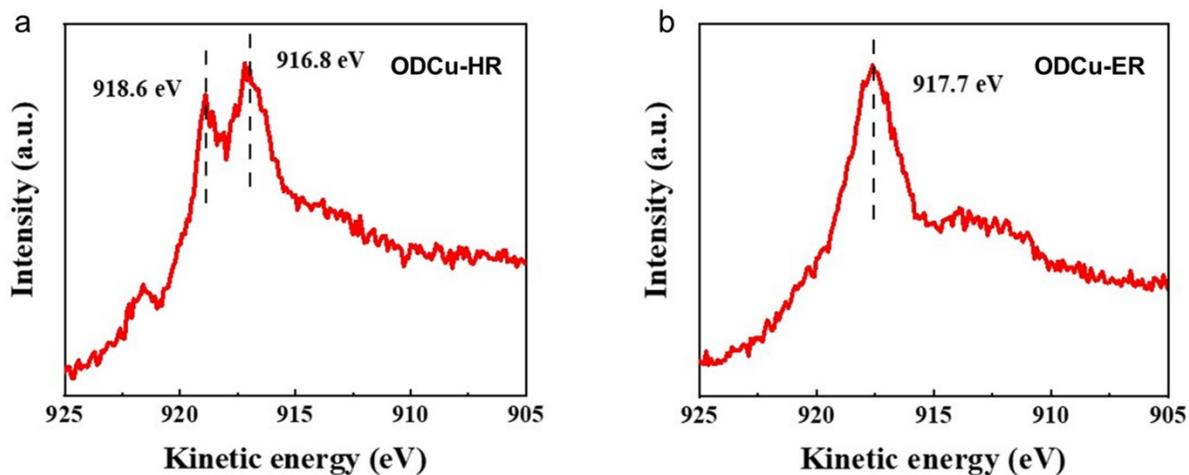


Figure S4. Cu $L_3M_{45}M_{45}$ Auger spectroscopy of (a) ODCu-HR (b) ODCu-ER. The peak at 918.6 eV, 917.7 eV and 916.8 eV are assigned to Cu (0), Cu (II) and Cu (I). In ODCu-HR, the sample surface is composed of Cu and Cu_2O , while in ODCu-ER, the sample surface maintains CuO , indicating that electrochemical reduction can retain more oxides and benefit the CO_2RR performance.