SUPPORTING INFORMATION

Electrochemical CO_2 Reduction on Cu_2O-dervied Copper Nanoparticles: Controlling the Catalytic Selectivity of Hydrocarbons

Experimental Methods

Faradaic efficiency calculation: The Faradaic efficiency (FE) of the CO_2 electrochemical reduction of products was calculated as

$$FE(\%) = \frac{n_i F \ \phi_i F_m}{I}$$

where n_i is the number of the electrons needed for CO_2 reduction, F is the Faraday constant, ϕ_i is the volume fraction of the gases, I is the current obtained and F_m is the molar CO_2 gas flow rate. The number of electrons associated with reduction are 2,8,12,14 for formation of CO, methane, ethylene, and ethane, respectively. The volume fraction of the gases is calculated by calibrating the gas chromatogram (GC) using a diluted mixture of gases of known concentrations.

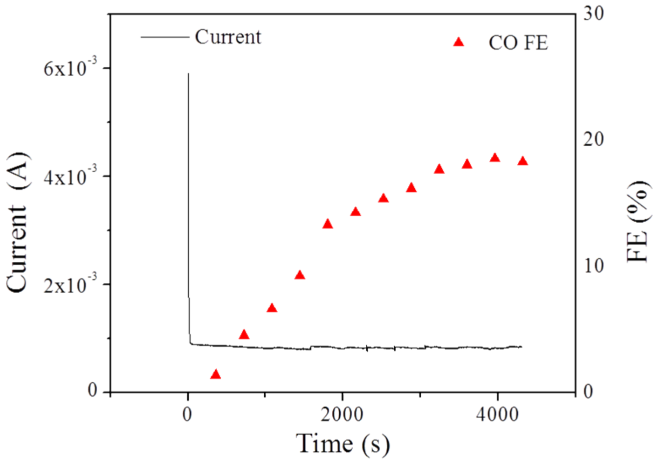

Figure SI1 The transient behavior of the electrochemical reactor at a constant applied potential. The time needed to reach steady state, applying a flow rate of 5 mL/min, was ~40 min, as evident from the trend in CO Faradaic Efficiency. All the CO_2 electrochemical reduction experiments were conducted for at least one hour, and steady state values are reported throughout the manuscript.

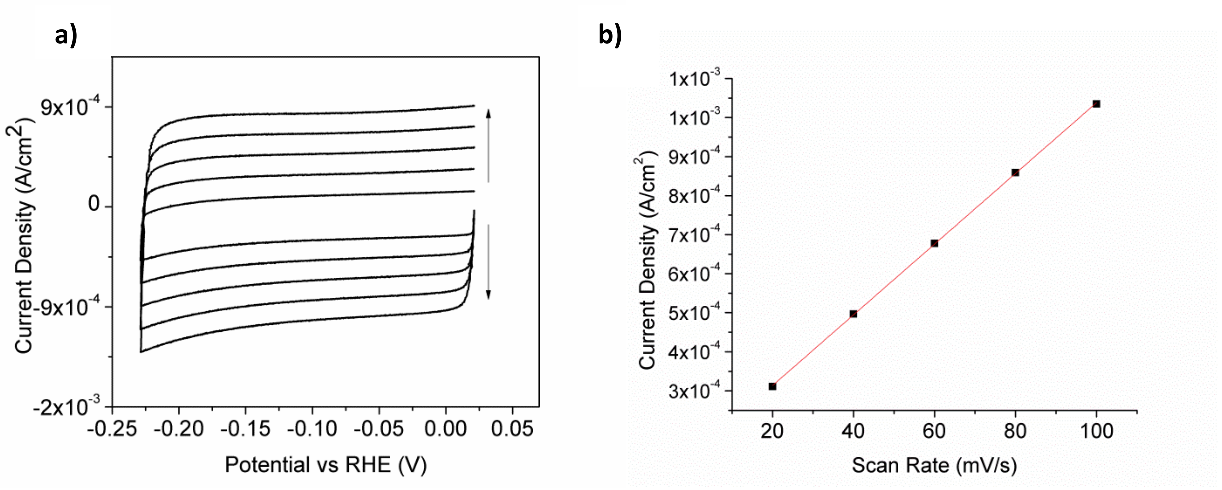

Figure SI2: a) CV curves of a nano-particulate Cu surface derived from an oxide film prepared at 11 C/cm^2. The arrows indicate the trends induced by an increase in scan rate. b) the current density vs. scan rate plot for the corresponding film.

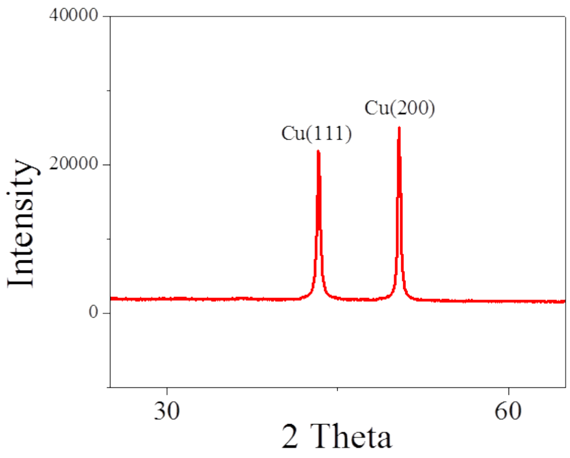

Figure SI3 The X-ray diffraction pattern of coatings after electrochemical reduction at -0.6 V vs RHE.

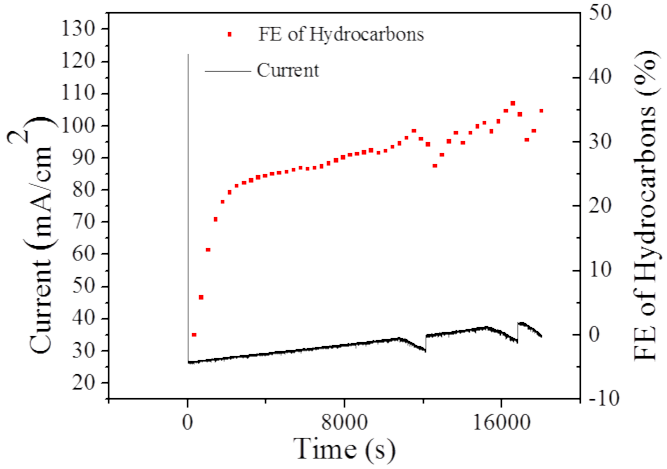

Figure SI4: Long term stability analysis for the thinnest sample (3 C/cm^2) at constant potential. The applied potential varies somewhat in time due to increasing resistance of the solution, in agreement with IR values determined before and after the experiment. The potential at the surface apparently fluctuates between -1.04 and -1.09 V vs RHE during the experiment.

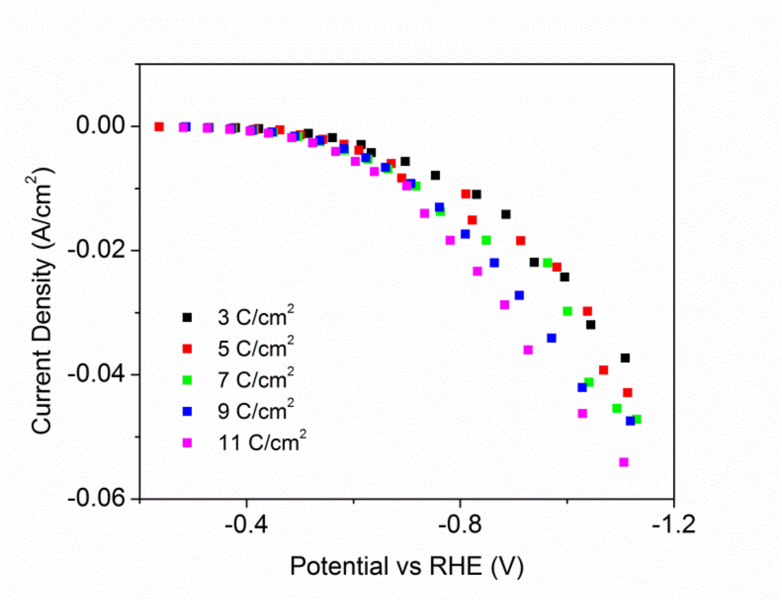

Figure SI5: The stable current density values obtained during electrochemical CO_2 reduction as a function of potential for different thickness of the oxides.

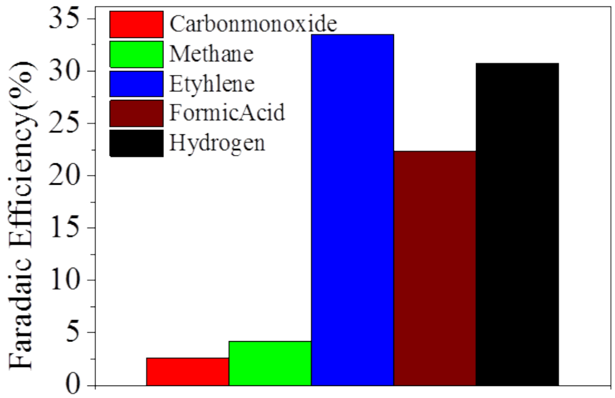

Figure SI6: Product distribution (FE (%)) for the thinnest sample (3C/cm^2), including the product Formic Acid, which was dissolved in the electrolyte and determined *ex situ* by HPLC.

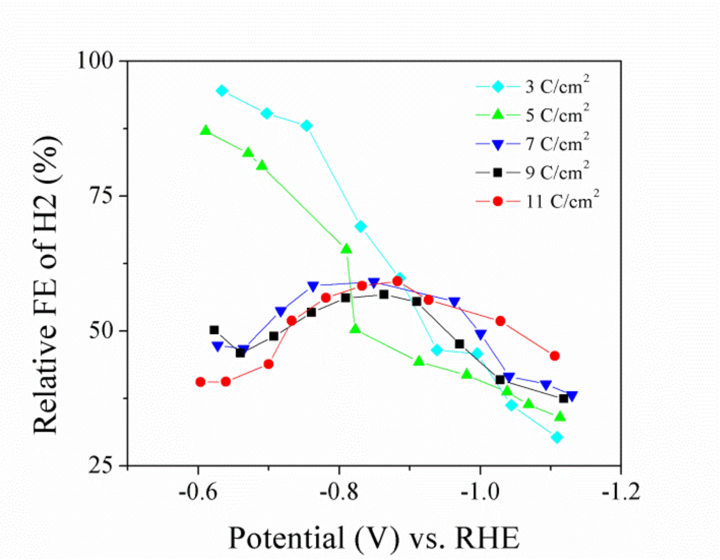

Figure SI7 : Relative FE of the Hydrogen evolution reaction as a function of initial oxide thickness