Supporting Information

Formation of 1-Butanol from CO_2 without *CO Dimerization on Phosphorus-Rich Copper Cathode

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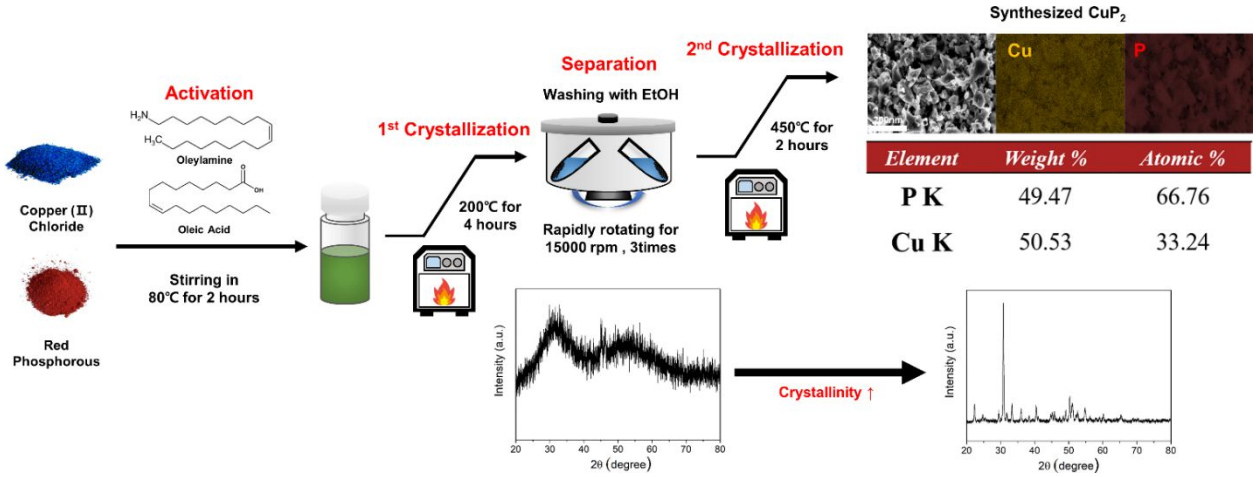
Experiment method

Preparation of catalyst



Scheme S1. Overall synthesis method of copper phosphide, separated by each step of activation, 1st & 2nd crystallization. SEM images with EDS mapping indicating the atomic ratio of Cu and P was 1:2.

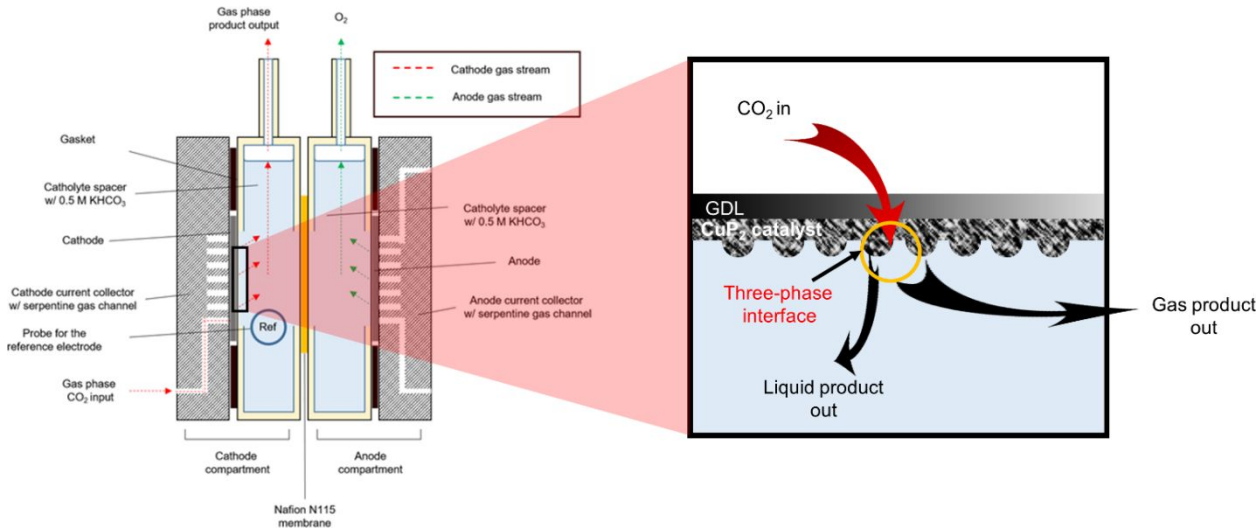
Oleate method was used for synthesizing copper phosphide particles.[1] Mixing $CuCl_2$ (Merck) and Red Phosphorous (Alfa Aesar, Phosphorous powder, -100 mesh, red amorphous 98.9%) to make each particle, synthesized it with its own weight ratio. The weight ratio in the content of copper in $CuCl_2$ and red phosphorous was 1:2. For activation of the complex, the powder mixture is then stirred in the solution oleic acid (Aldrich, technical grade, 90%) and oleylamine (Aldrich, technical grade, 70%) in the volume ratio of 1:1 for 2 hours in 80 ℃. Next, for the first crystallization, the catalyst was heat-treated at 200 ℃ for 4 hours under N_2 atmosphere, through an increasing rate of temperature was controlled at 5 ℃/min by the automated tubular furnace. After 4 hrs, the samples were naturally cooled down at room temperature. Separation of oleic acid and oleylamine from the sample was carried out by washing with ethanol using the centrifuge at 15,000 rpm three times.

The process of throwing away the supernatant liquid and filling it with ethanol was repeated. Finally, to increase the crystallinity of the amorphous particles after the first crystallization, additional heat treatment at 450 ℃ for 2 hrs was progressed.

Characterization of the synthesized electrocatalyst.

X-ray Diffraction (XRD, Rigaku Miniflex Ⅱ) equipped with Cu Ka (0.15406 nm) X-ray source, was used to investigate the crystal structures and surface compositions of each sample of different heat-treatment temperature. The distribution and morphology changes of each sample before and after CO_2 reduction was observed with Field-Emission Scanning Electron Microscope (FE-SEM, S-4700, Hitachi). For further analysis of the elemental compositions, Energy-Dispersive X-ray Micro-analysis (EDS) mapping was simultaneously performed. To precisely analyze the surface characteristic of each element, X-ray Photoelectron Spectroscopy (XPS, Theta Probe AR-XPS system), equipped with the Al Ka X-ray source (1486.6 eV), was used for elemental analysis in Busan center of Korea Basic Science Institute (KBSI).

Electrolysis experiments



Scheme S2. Schematic illustration and operating principle of the continuous-flow CO_2 Electrolyzer 2D illustration of the cell and schematic composition of three-phase interface on the cathode surface.

Continous-flow electrochemical conversion cell configuration.

To separate the catalyst layer and the cation exchange membrane, an electrolyte holder capable of forming a buffer layer between the membrane and the catalyst layer was devised. An acrylic chamber that is 24 mm thick with a 3 cm x 3 cm window was made. Between 2 mm thick acrylic sheets with 3cm x 3cm window, 20 mm thick acrylic sheet with 5 cm x 5 cm window was placed to make a totally 24 mm thick electrolyte cell. Between the anode and cathodes catalyst layers, 2 electrolyte chambers were placed separated by a cation exchange membrane. Behind the cathode, a graphite flow channel for CO_2 to flow through the electrode was placed. On the other side of the anode, the same graphite flow channel was placed opened that the evolved O_2 could escape out of the cell. On the electrolyte holder of the cathode side, an L-shaped probe was placed for the reference electrode to establish a three-electrode system. A brass current collector was placed

behind each graphite to act as a current collector for potentiostat/galvanostat. To hold the entire cell together, 8 insulated bolts were tightened.

Surface analysis of in-situ surface-enhanced infrared adsorption spectroscopy (SEIRAS).

Au layer for conductivity was prepared by electroless deposition technique similar to a couple of previous studies.[2,3] A triangular Si prism (Pier Optics, Japan) was polished using alumina solution (Al_2O_3 > 99.8%, Sigma Aldrich, primary 13 nm powder) and then rubbed under flowing of deionized water (18 MΩ). After polishing, the Si prism was immersed in 40% NH_4F solution (Sigma Aldrich) for ~20 sec to form a hydrophobic etched Silicon surface, which is then immersed in the mixture of Au plating solution composed of 0.015 M Sodium Tetrachloroaurate(Ⅲ) Dihydrate ($Na(AuCl_4)\cdot 2H_2O$, Sigma Aldrich), 0.15 M Sodium Sulfite (Na_2SO_3, Wako), 0.05 M Sodium Thiosulfate Pentahydrate ($Na_2S_2O_3\cdot 5H_2O$, Wako), 0.05 M Ammonium Chloride (NH_4Cl, Wako) and 2% Hydrogen Fluoride (HF, Sigma Aldrich). The Au electroless deposition proceeded for 70 sec at 55 ℃. After the Au electroless deposition, the catalyst ink was deposited above the Au layer by a drop-casting method. Deionized water was added for using the surface tension of the water in order to make the area through drop-casting more in a circle. After the drop-casting, the ink was dried in the oven 60 ℃ for 20 min. Finally, the catalyst electrode is assembled for an in-situ SEIRAS electrochemical experiment

All electrochemical measurements used a potentiostat/galvanostat (PGSTAT-302N, Autolab) are expressed versus the reversible hydrogen electrode (RHE). CuP_2 was drop-casted above the electroless deposited Au layer. Ag/AgCl was used as a reference electrode, and Pt mesh worked as a counter electrode. After the catalyst-deposited Si prism is ready, it was assembled with an electrochemical cell for the SEIRAS experiment. 0.5 M Potassium Bicarbonate ($KHCO_3$, Sigma

Aldrich) solution was used as electrolyte buffer for CO_2 reduction. A Fourier Transform Infrared Spectrometer (FT-IR, Cary 670, Agilent) equipped with a MCT detector and a handmade single reflection accessory was used to obtain SEIRA spectra. Before every experiment of SEIRAS assembled with an electrochemical test, linear sweep voltammetry (LSV) scans were performed at a scan rate of 10 mV sec^{-1} to electrochemically reduce surface oxides with continuous N_2 (99.999%) purging. After the cleaning process of the surface, the catalytic activity of electrochemical CO_2 reduction was evaluated through linear sweep voltammetry in 0.5 M $KHCO_3$ electrolyte with N_2, CO_2 and CO bubbling, respectively.

Product Analysis.

For the composition analysis of gas-phase products, 300µl of sampled gas was loaded into an impact syringe and flowed directly into the Gas chromatograph and Mass Spectroscopy analyzer. Hydrogen was analyzed by Gas Chromatography (GC, Agilent 7890A, Agilent Technologies) with a thermal conductivity detector (TCD) and other Hydrocarbons were analyzed by Gas Chromatography-Mass Spectrometry (GC-MS, Agilent Technologies) with GS-GASPRO column (Agilent Technologies) at column temperature in the range of 298 K to 330 K at a ramping rate of 5 K min^{-1}. Hydrogen (H_2) was observed at the retention time of 1.69 min and other gas products CO (1.3 min) was observed in GC-MS. In addition, Headspace sampler (Agilent 7697A, Agilent Technologies) with HP-INNOWAX column (Agilent Technologies) quantified liquid phase products, such as acetaldehyde and 1-butanol. Additional product analysis was carried out with NMR experiments, performed using a 600 MHz spectrometer (Bruker Advance Neo) equipped with a liquid-nitrogen-cooled TCI NMR probe. 1-D ^1H spectra of each product were collected at 298 K with a solvent suppression pulse sequence (zgesgp). One pulse experiment was in a

condition of $\pi/2$ pulse of 7.5 μs and a recycle delay time of 1 s was implemented for 4096 scans per experiment.

Characterization of electrochemical reduction of CO_2

Fabrication of electrodes.

The gas diffusion layer (29 BC, Ion power), a non-woven carbon paper with a microporous layer that has been PTFE treated, was used as a carbon substrate. For both anode and cathode electrodes, the air-brush method was used. Each electrode was the size of 3 cm x 3 cm. On the anode, the ink was composed of 17.3 mg Pt/C catalyst (TEC10C50E, Tanaka), 13.87 mg Nafion solution (10 wt. % in H_2O, Sigma-Aldrich), 1750 mg isopropyl alcohol, and 173.4 mg deionized water. The ink was composed of 27 mg synthesized catalyst, 27 μl Nafion solution, and 7860 mg isopropyl alcohol on the cathode. Each anode and cathode ink mixture was sonicated for 1 hour. Weighing the carbon substrate before/after forming the catalyst layer, 0.5 mg Cu-P/cm^2 was loaded. For the CO_2 reduction experiment, 0.5 M Potassium Bicarbonate ($KHCO_3$, Sigma Aldrich) solution was used as electrolyte buffer for CO_2 reduction. The CuP_2 catalyst was air-brushed onto the gas diffusion electrode (GDE) while, Pt/C was air-brushed as an anode with the same procedure. The working electrode and counter electrode had a large surface area (9 cm^2) in a catholyte (75 mL) and anolyte (70 mL).

Electrochemical reduction experiment.

Potentiostat/galvanostat (PGSTAT30, Autolab) was used to control the cathode potential and measure the resulting current. A cation exchange membrane (Nafion 115, DuPont) was used as a separator between anode and cathode compartments. CO_2 reduction and Oxygen evolution

reaction is a relatively slower reaction and has high overpotential, so it is hard to acquire accurate cathode potential with a two-electrode system. To complement, a three-electrode system was constructed using Ag/AgCl as a reference electrode. The reference electrode can provide the accurate potential of the cathode aside from electrochemical reaction. All experiments were done in ambient pressure and temperature. The CO_2 gas was controlled by a gas flow controller and the flow rate was fixed in 30 sccm (ml/min).

The electrochemical reduction experiment was carried out at constant potential for 2 hours, to compare with each potential. According to Nernst Equation, all the electrode measured potentials were converted in relatively Reversible Hydrogen Electrode (RHE). The following equation was used to convert the electrochemical data obtained from the Ag/AgCl reference electrode to RHE.

$$E_{RHE} = E_{Ag/AgCl} + 0.210\ V + 0.059 \times pH$$

E_{RHE}: calculated cathode potential converted in RHE scale.

$E_{Ag/AgCl}$: measured cathode potential potential by Ag/AgCl reference electrode

pH: pH value of the liquid electrolyte

For the evaluation, faradaic efficiency (FE) was calculated to identify how efficiently the current applied to the electrochemical cell was assigned to the desired electrochemical CO_2 reduction reaction.

$$FE_A = \frac{Q_A}{Q}$$

FE_A: Faradaic Efficiency toward product A

Q_A: Partial Charge participating in the formation of A in coulombs

Q: Total electric charge applied to the electrochemical cell

The total electric charge (Q) is calculated by the sum of current as follows:

$$Q = \int_0^t I(\tau) d\tau$$

t: Total operation time of the electrochemical reduction reaction

The partial electric charge is calculated according to the physical law of electrochemistry as follows:

$$Q_A{:}n_A \cdot F \cdot z$$

n_A: Product A in mole

F: Faraday constant (96485 C/gmol)

z: Valency number of electron of the electrochemical reaction

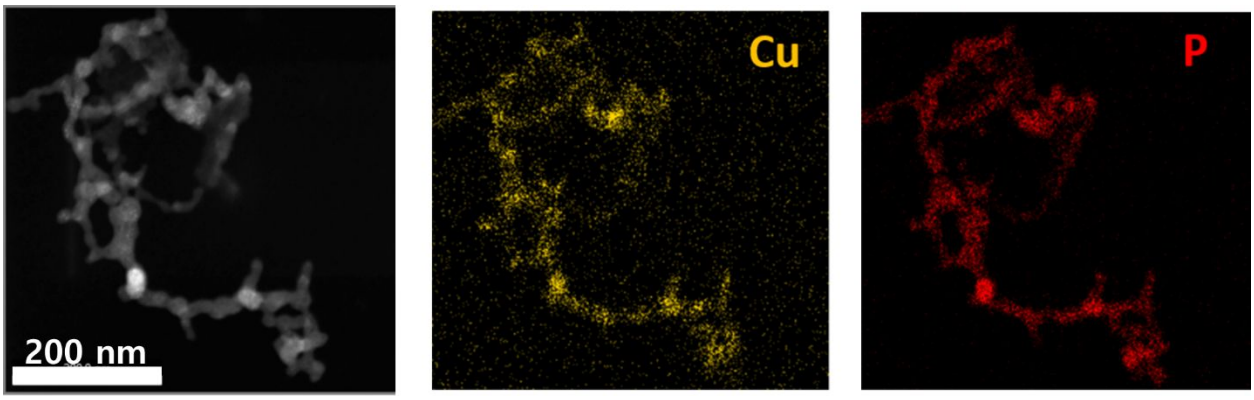


Figure S1. TEM-EDS image of CuP_2 and elemental mapping of copper (yellow) and phosphorus (red).

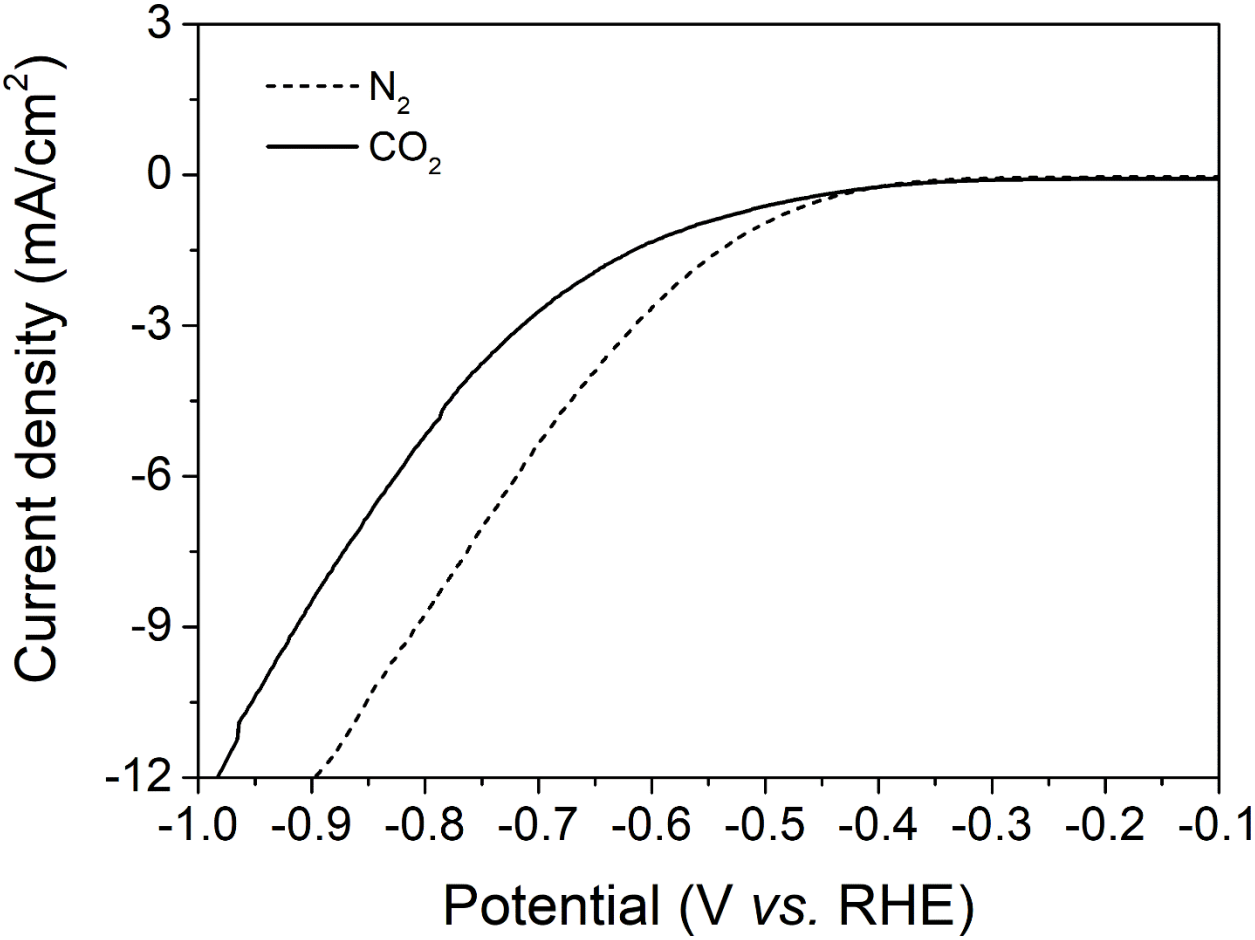


Figure S2. Linear sweep voltammograms in N_2 and CO_2 saturated 0.5M $KHCO_3$ at a scan rate of 10 mV s^{-1}.

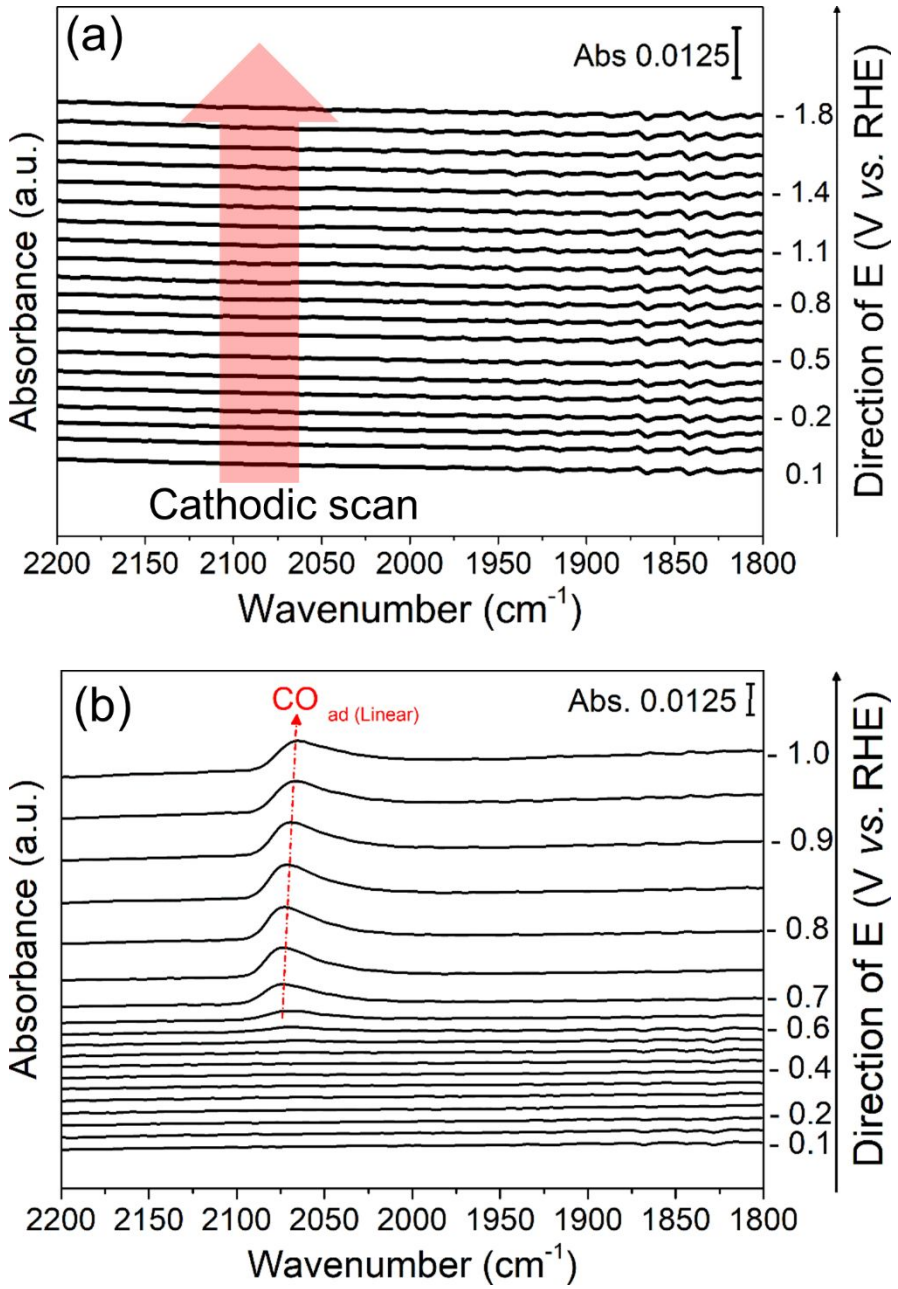


Figure S3. (a) *in-situ* SEIRA spectra acquired during CO reduction on CuP_2 surface during linear sweep voltammetry in a voltage range from 0.1 V_{RHE} to -1.8 V_{RHE} at intervals of ~100 mV. (b) *in-situ* SEIRA spectra acquired during CO_2 reduction on Cu surface during linear sweep voltammetry in a voltage range from -0.1 V_{RHE} to -1.0 V_{RHE} at intervals of ~50 mV

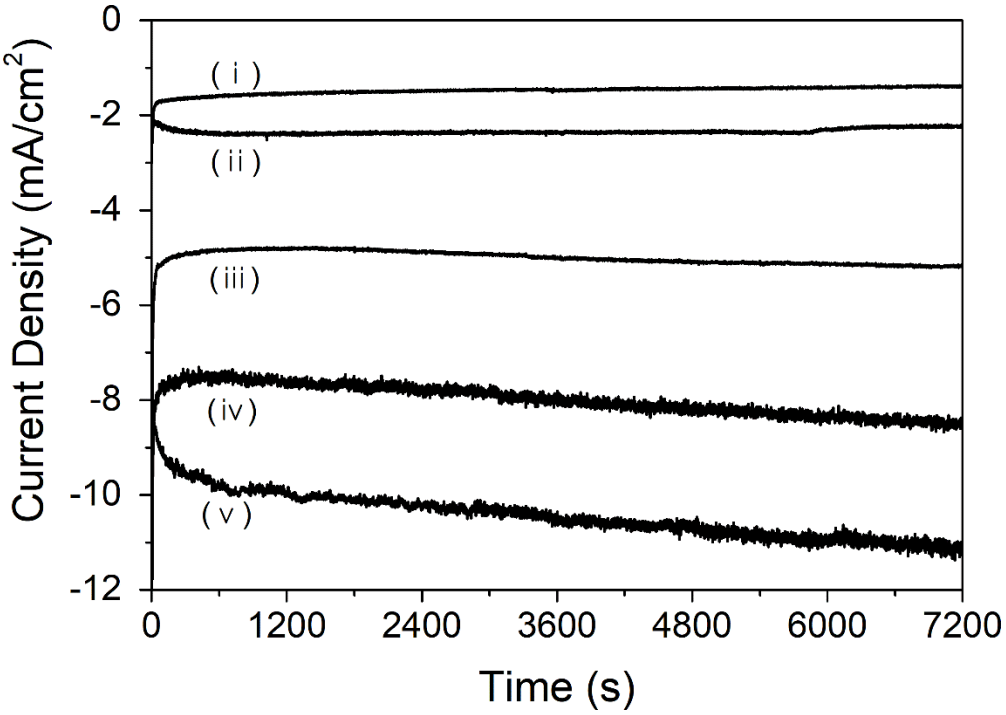


Figure S4. Representative chronoamperometry measurements at each potential of of (i) -0.5 V, (ii) -0.6 V, (iii) -0.7 V, (iv) -0.8 V, (v) -0.9 V as RHE scale for 2 hours on CuP_2 electrode.

Table S1. Faradaic efficiency of CO_2RR products in -0.6 V_{RHE} and -0.9 V_{RHE} potential using CuP_2 electrode

	Hydrogen (%)	Carbon Monoxide (%)	Formate (%)	Acetaldehyde (%)	1-Butanol (%)
-0.6 V_{RHE}	40.13 ± 5.84	0.55 ± 0.18	30.68 ± 3.86	22.71 ± 2.76	3.87 ± 0.66
-0.9 V_{RHE}	63.77 ± 4.86	0.14 ± 0.03	8.40 ± 1.76	22.39 ± 1.94	0.02 ± 0.01

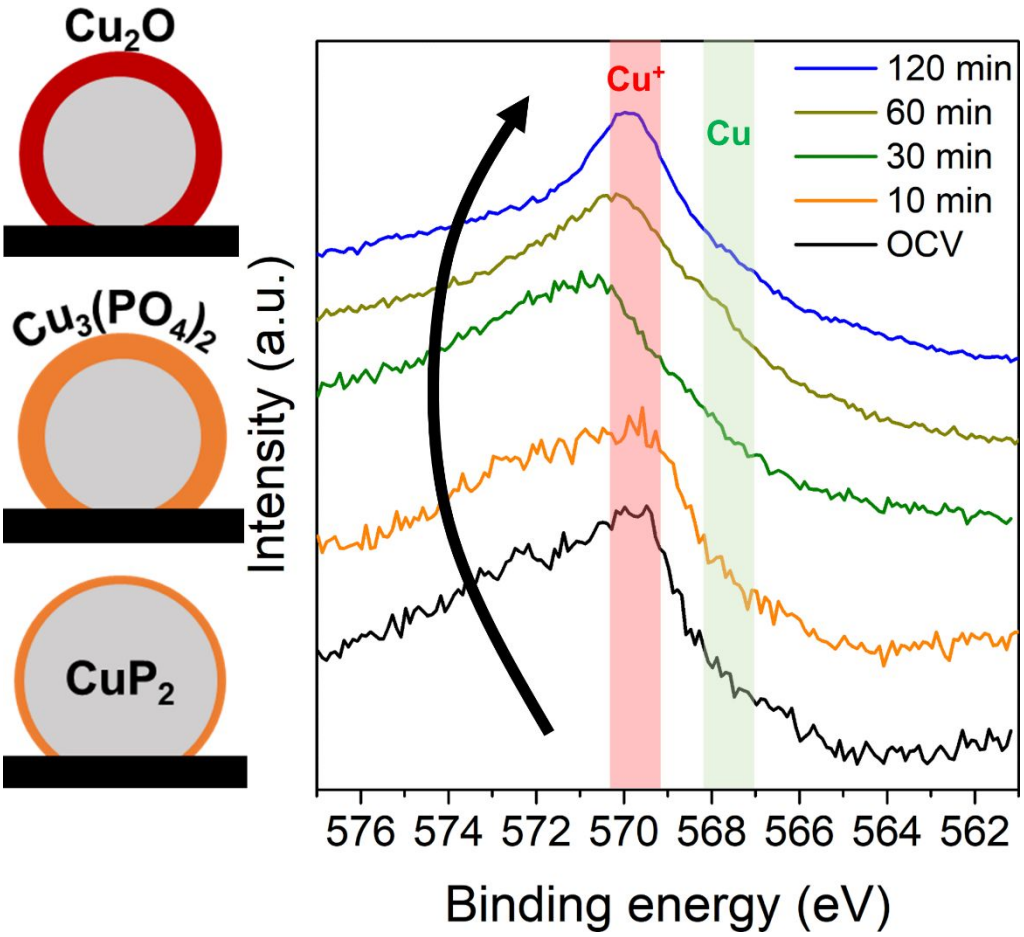


Figure S5. Time-resolved Cu LMM Auger spectra measured while CO2RR of time of OCV, 10 min, 30 min, 60 min, and 120 min. The red region represents the oxidation state of Cu^{+} and green region for Cu^{0}.

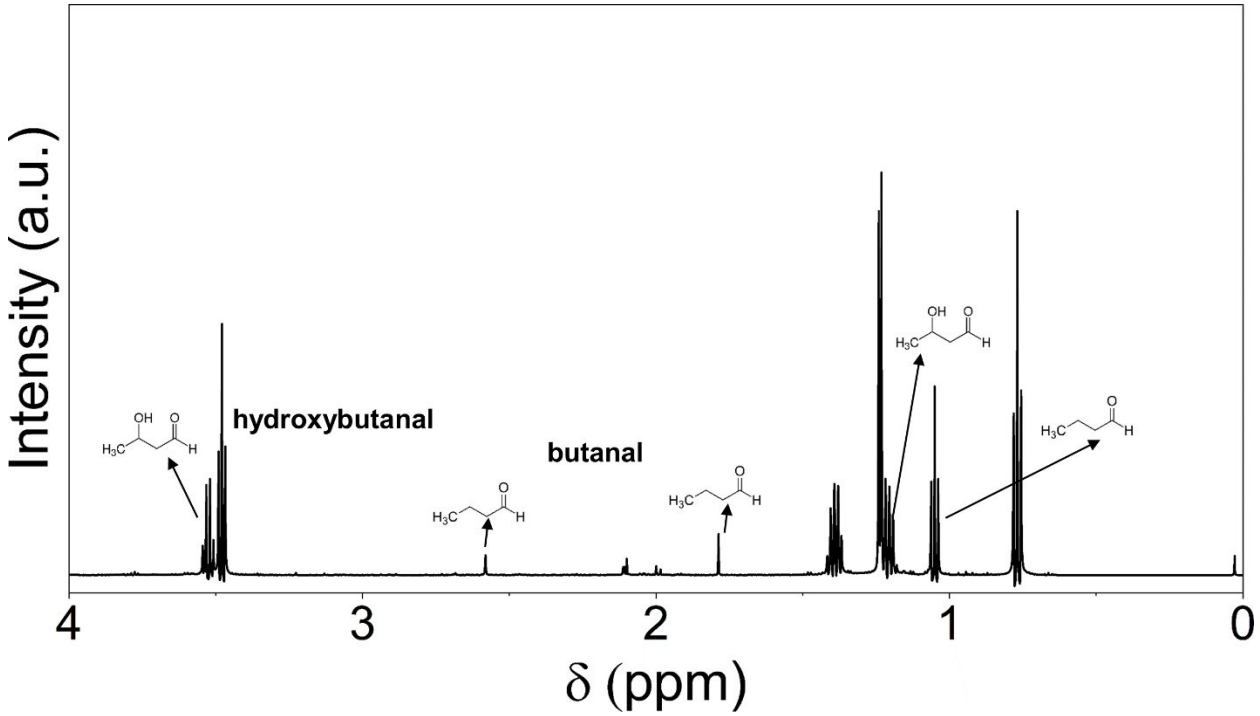


Figure S6. ^{1}H-NMR (600 MHz, D_2O) spectra of intermediates from aldehyde and aldol condensation reaction.

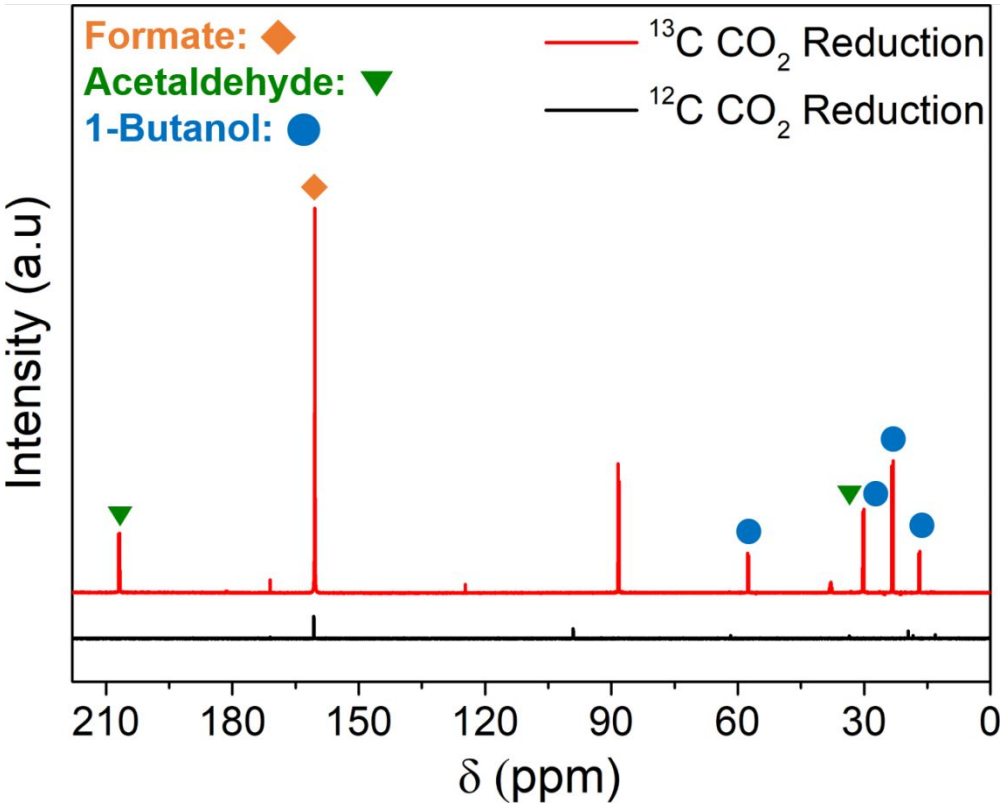


Figure S7. ^{13}C-NMR (600 MHz, DMSO) spectra of formate, acetaldehyde, and 1-butanol from ^{13}CO2 and ^{12}CO2 reduction after bulk electrolysis at –0.6 V_{RHE}.

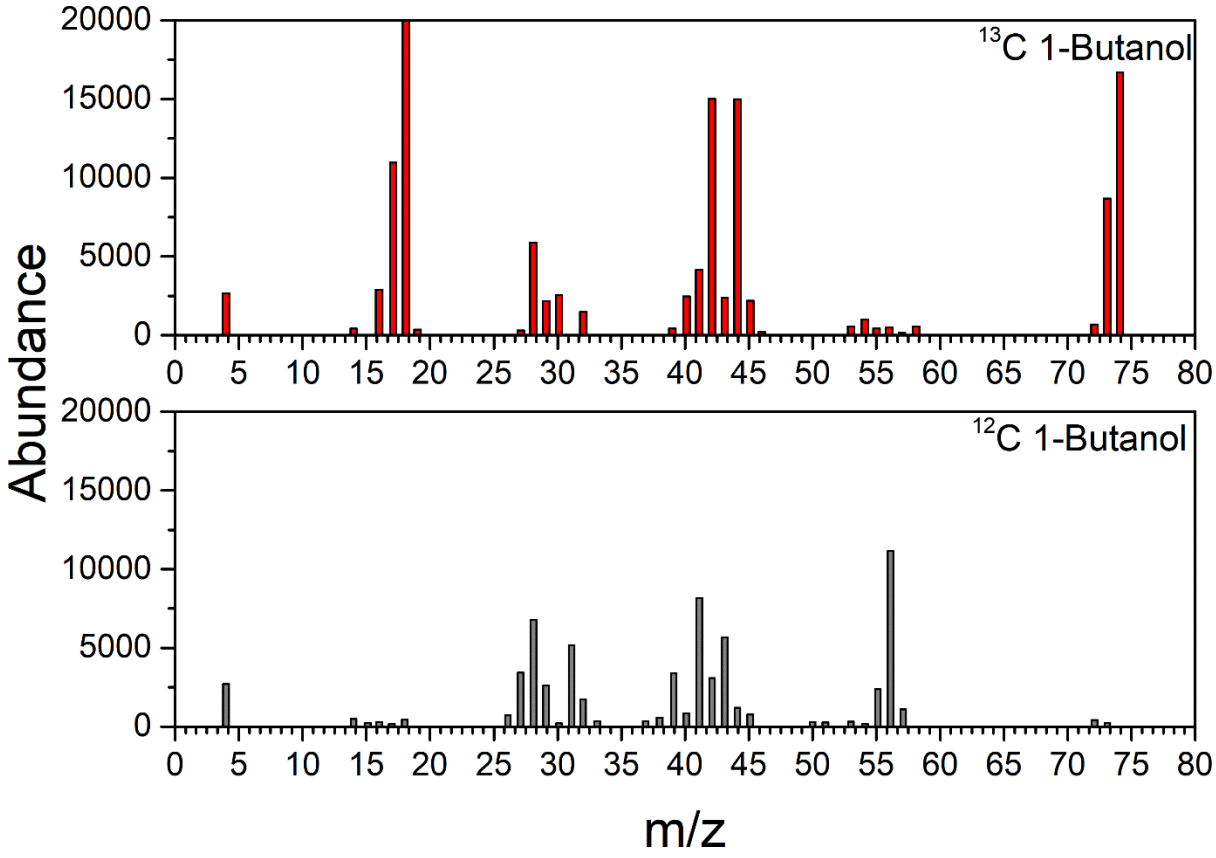


Figure S8. Headspace GC-MS spectrum of $^{12}CO_2RR$ and $^{13}CO_2RR$ after bulk electrolysis at -0.6 V_{RHE}.