

Electronic Supplementary Information (ESI) for

Electrochemical CO₂ reduction over nanoparticles derived from oxidized Cu-Ni intermetallic alloy

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Experimental section

Materials

All starting materials were used as-received. Hexane and potassium bicarbonate (KHCO₃) were purchased from Fujifilm Wako Pure Chemical Corp. Potassium bicarbonate-¹³C (KH¹³CO₃, 98 at% ¹³C) was purchased from Isotec Inc. Carbon paper (CP; TGP-H-060) was purchased from Toray Industries, Inc. Cu foil (99.9%, thickness: 0.08 mm) and cupronickel (Cu:Ni=70:30, thickness: 0.3 mm) foil were purchased from Nilaco Corp.

Synthesis of Cu-Ni NPs

Cu-Ni nanoparticles (NPs) with various composition (0-83 at%-Ni) were just used as synthesized and characterized in a previous report.¹ Cu-Ni NPs were synthesized by using a one-pot and a two-step process. First, a dispersion of Cu seeds was obtained by heating a mixture of 30 mmol oleylamine (Aldrich, 70%) and 1.7 mmol copper (II) acetylacetonate (Stream Chemicals, >98%) to 200 °C for 1 h under a N₂ flow. After cooling the mixture to room temperature, 0-7.2 mmol of Ni (II) chloride (Tokyo Kasei, >98%) and 2.4 mmol of trioctylphosphine (Wako, >96%) were then added to the Cu

seed dispersion, and the liquid portion was subsequently removed and the mixture dried in a vacuum. The particles were stored in a vacuum desiccator (as-synthesized Cu-Ni NPs). The particles were naturally oxidized by leaving them in the air at room temperature for months (oxidized Cu-Ni NPs).

Preparation of Cu-Ni NPs on carbon paper (CP)

Cu-Ni NPs (12 mg) were mixed in hexane (1 mL) and dispersed for 30 min by high frequency ultrasonication. The NP suspension (50 μ L) was dropped onto the CP (1.8 \times 2.5 cm, coating area; *ca.* 1.0 \times 1.8 cm), followed by drying at room temperature. The coating procedure was repeated 3 times and the resultant Cu-Ni NPs/CP was dried under vacuum at 40 $^{\circ}$ C. In this manner, a 0.2 mg quantity of the Cu-Ni NPs was loaded on each 1.8 cm² of the CP.

Electrochemical measurement for the CO₂ reduction (CO₂Rs)

A potentiostat (ALS612E, BAS) was used for the electrochemical CO₂R measurement. The sample electrode (1 \times 1.8 cm), platinum wire, and a silver/silver chloride electrode (Ag/AgCl: RE-1S, BAS Inc.) were used as the working, counter, and the reference electrodes, respectively. A Pyrex sealed glass cell (total volume: 123.6 mL) was used as a one-compartment reactor, and 0.05 M KHCO₃ aqueous solution (50 mL) saturated with CO₂ (pH 6.9) was used as an electrolyte. The amounts of CO, H₂ and CH₄ in the gas phase were determined using gas chromatography (GC-2014, Shimadzu Corp.) equipped with an active carbon column. The amounts of gaseous CH₄, C₂H₄, C₂H₆, C₃H₈ and C₃H₆ were determined using gas chromatography (GC-2010 plus, Shimadzu Corp.) equipped with a GS-Q column. The amount of HCOO⁻ in the solution was determined using ion chromatography (ICS-211, Dionex Corp.) with IonPacAS15 and IonPacAG15 columns. The amounts of CH₃OH and C₂H₅OH in the solution were determined using gas chromatography-mass spectrometry (GC-MS; GCMS-QP2010, Shimadzu Corp.) equipped with a DB-BAC2 UI column. The amounts of products in the gas phase and the solution were quantified every hour, and the current efficiency was calculated. The CP background signal was subtracted. These efficiencies were measured for at least 3 electrodes for each

composition to ascertain reproducibility.

Characterization

Field emission scanning electron microscopy (FE-SEM) observations were made using an S-5500 microscope (Hitachi High-Tech Corp.). The crystal structures of the samples were assessed using X-ray diffraction (XRD; Ultima IV, Rigaku Corp.) with Cu K α radiation at 40 kV and 40 mA. Dark field scanning transmission electron microscopy (DF-STEM) and transmission electron microscopy (TEM; JEM-2100F, Joel) observations were conducted at an acceleration voltage of 200 kV. The average particle sizes in test samples were calculated from the sizes of 70 particles in an STEM image. The components of the Cu-Ni NPs on the CP were determined using inductively coupled plasma-mass spectrometry (ICP-MS; Agilent 8800, Agilent Technologies, Inc.). The chemical states of Cu and Ni were evaluated using X-ray absorption fine structure (XAFS) spectroscopy. Cu and Ni K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were acquired in the fluorescence mode using the BL16XU and BL16B2 beamline at Spring-8 (Hyogo, Japan). The Fourier transforms (FT) were done in the k -range of 2-8, and k -weight of 2, and they indicate the radial-structure function (RSFs) of the Cu or Ni atoms.

Isotope analysis

Isotope experiments for the electrochemical reduction over activated Cu-Ni (19 at%-Ni) were conducted using $^{13}\text{CO}_2$ (99 at% ^{13}C , ISOTECH) in 0.05 M $\text{KH}^{13}\text{CO}_3$ aqueous solution at -1.2 V (vs. RHE) for 3 h. ^{13}CO , $^{13}\text{CH}_4$, and $^{13}\text{C}_2\text{H}_4$ obtained by the electrochemical CO_2RR were detected using GC-MS (7890B and 5977B, Agilent Technologies, Inc.) equipped with a CARBONPLT column.

Results

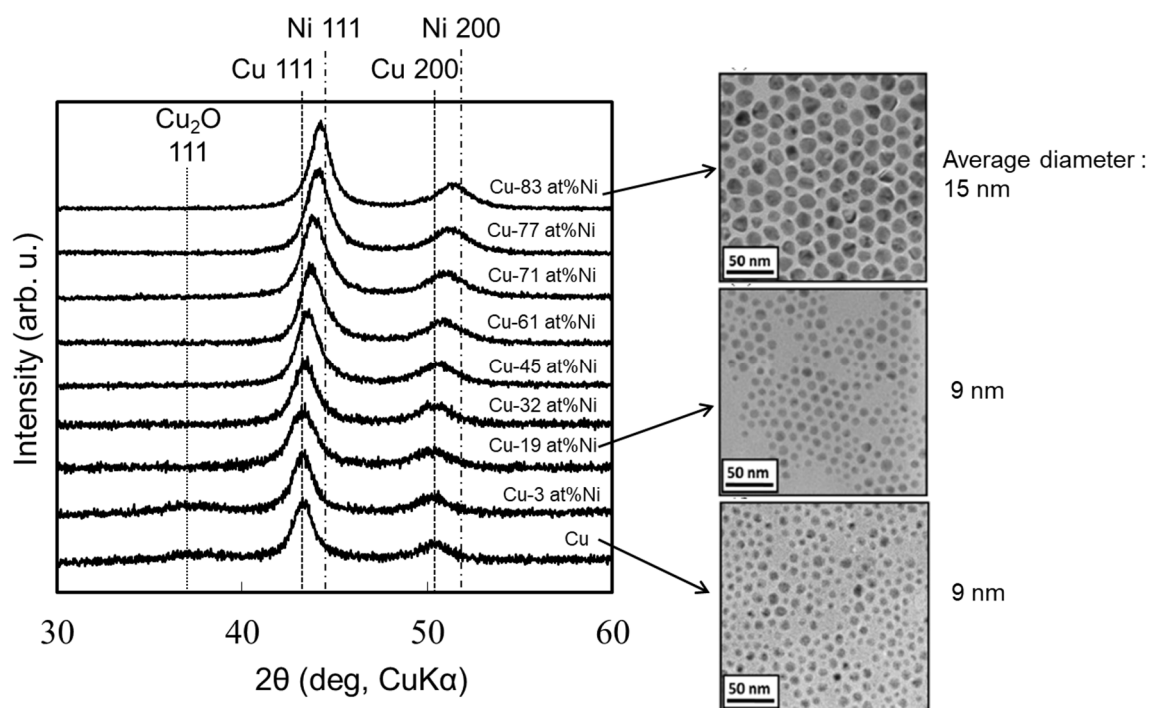


Fig. S1 XRD patterns and TEM images of as-synthesized Cu-Ni nanoparticles (Cu-Ni NPs). ¹

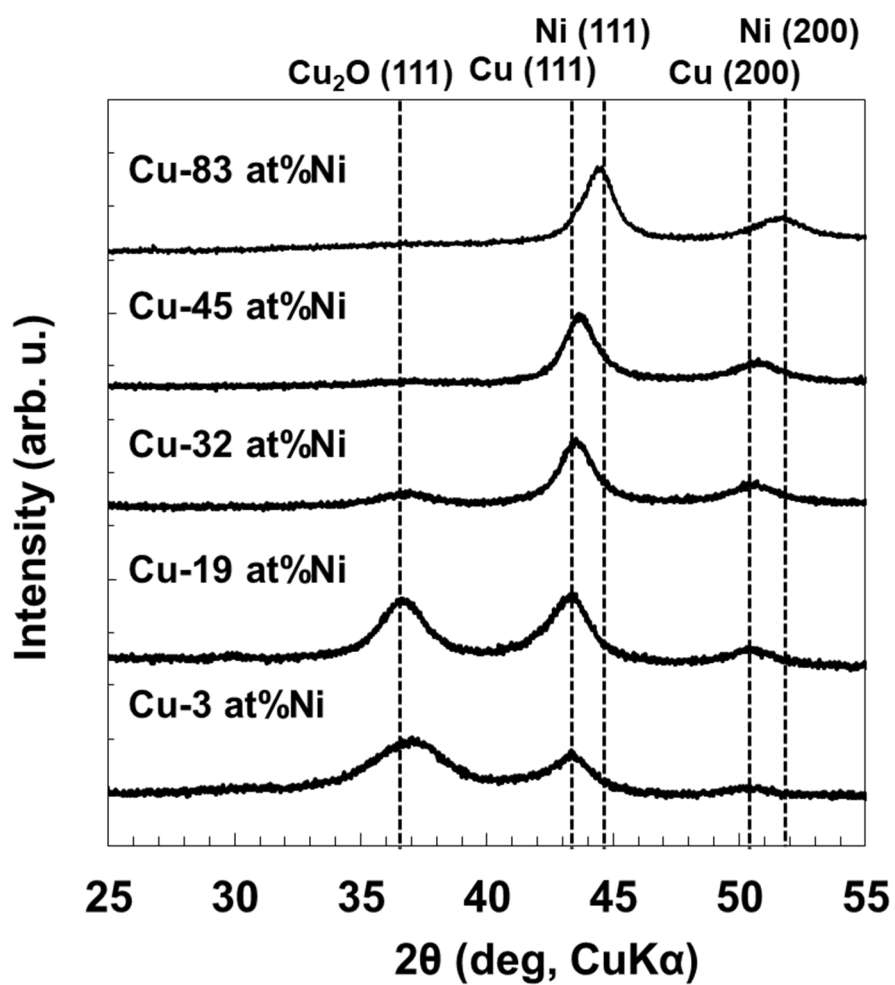


Fig. S2 XRD patterns of naturally-oxidized Cu-Ni NPs (oxidized Cu-Ni NPs).

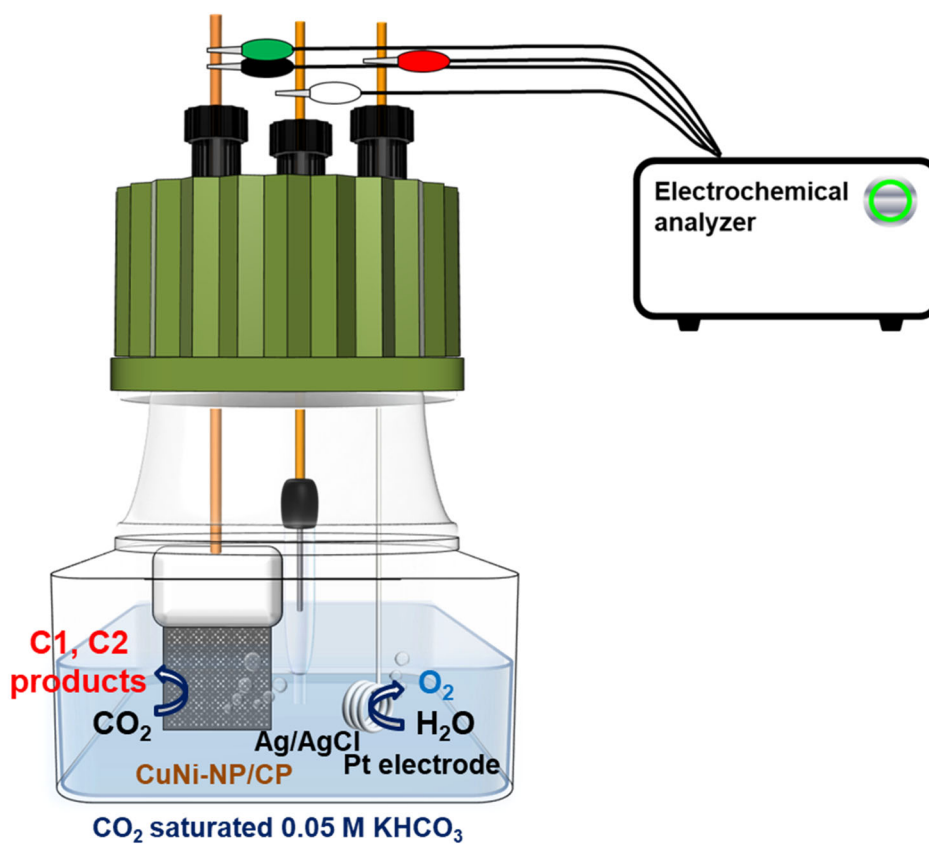


Fig. S3 Schematic illustration of electrochemical CO₂ reduction using a CuNi-NP/CP with a three-electrode system, measured in a CO₂-saturated 0.05 M KHCO₃ aqueous solution (pH 6.9).

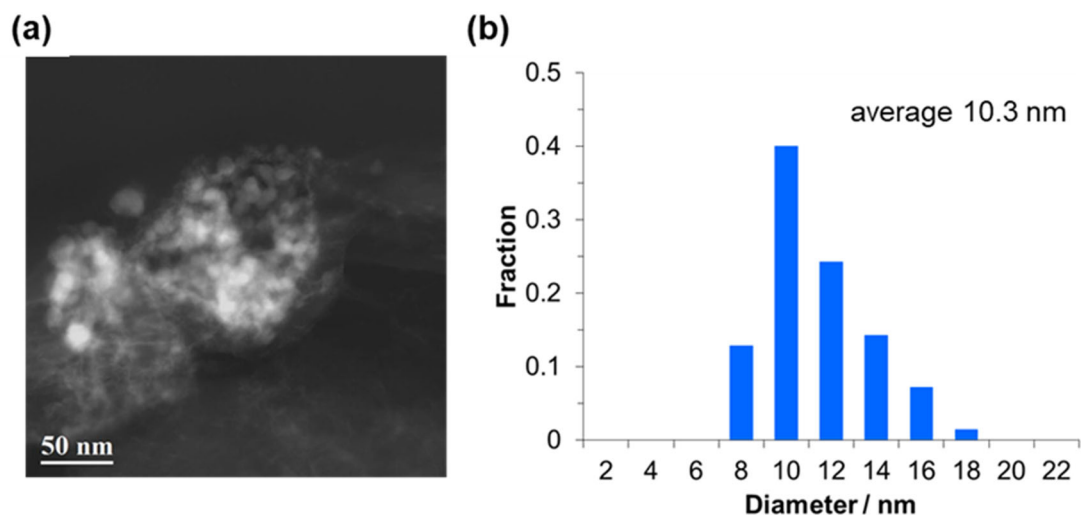


Fig. S4 (a) DF-STEM images of activated Cu-19 at% Ni NP and (b) particle size distribution obtained from STEM images.

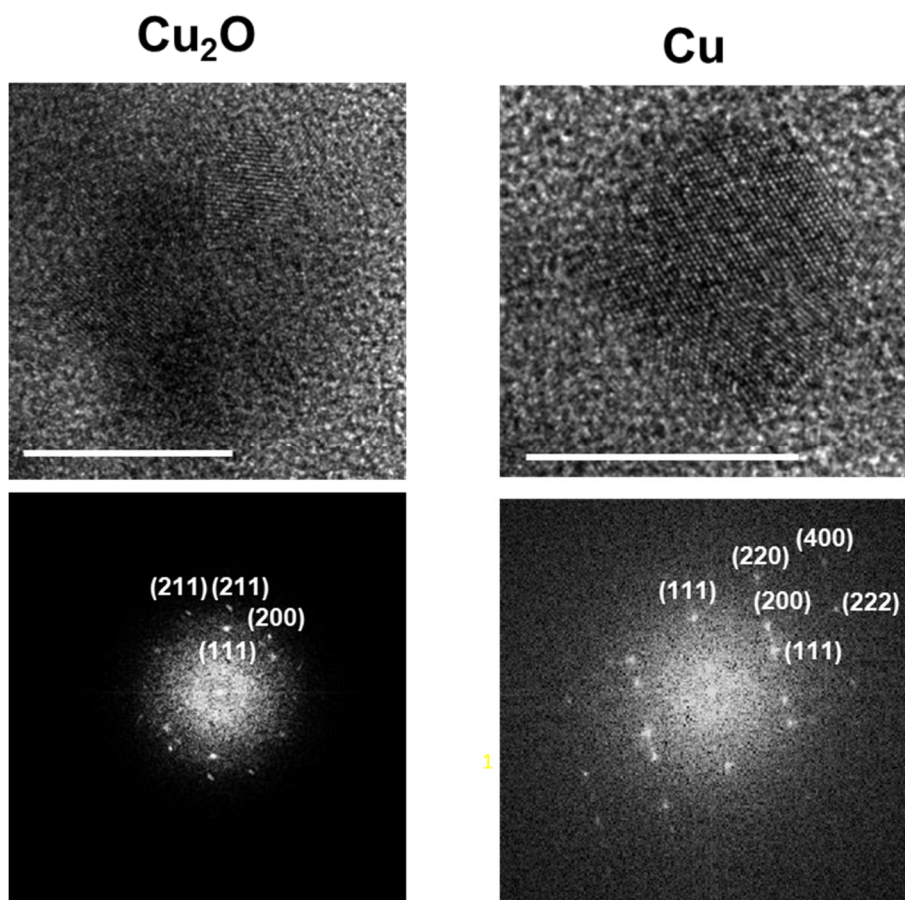


Fig. S5 High-resolution TEM images of activated Cu-19 at% Ni NP containing Cu_2O and Cu, and their fast Fourier transforms (FFTs). Scale bar: 10 nm.

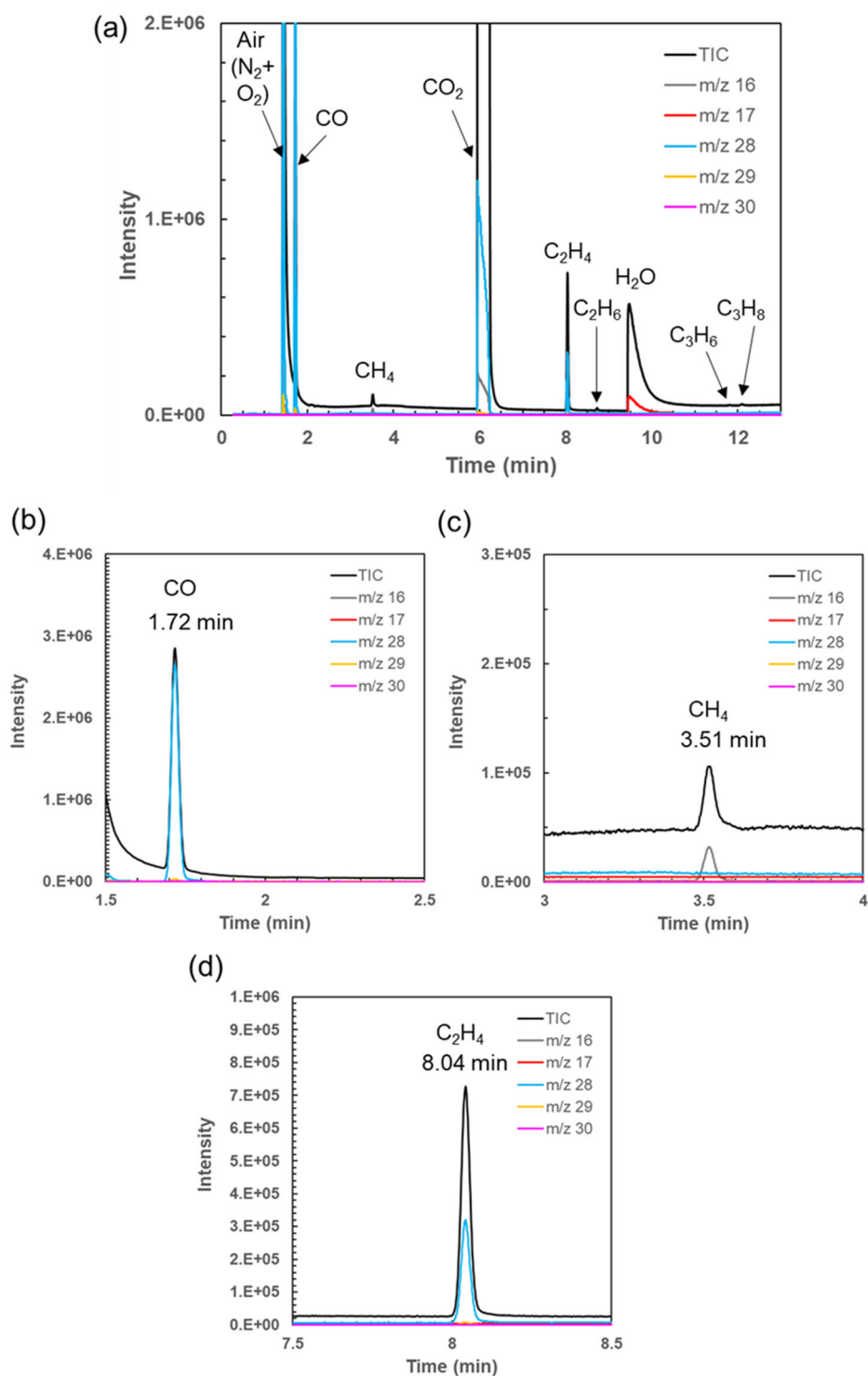


Fig. S6 Total ion current (TIC) chromatogram and extracted ion chromatogram (EIC) of gas products CO₂ electrochemical reduction over activated Cu-19 at% Ni NP/CP obtained by GC-MS (in CO₂-saturated 0.05 M KHCO₃ at -1.2 V vs. RHE for 3 h): (a) overall chromatogram (retention time 0-13 min), (b) CO (1.72 min, *m/z* 28 signal), (c) CH₄ (3.51 min, *m/z* 16 signal), and (d) C₂H₄ (8.04 min, *m/z* 28 signal). For GC-MS spectra see Fig. S8.

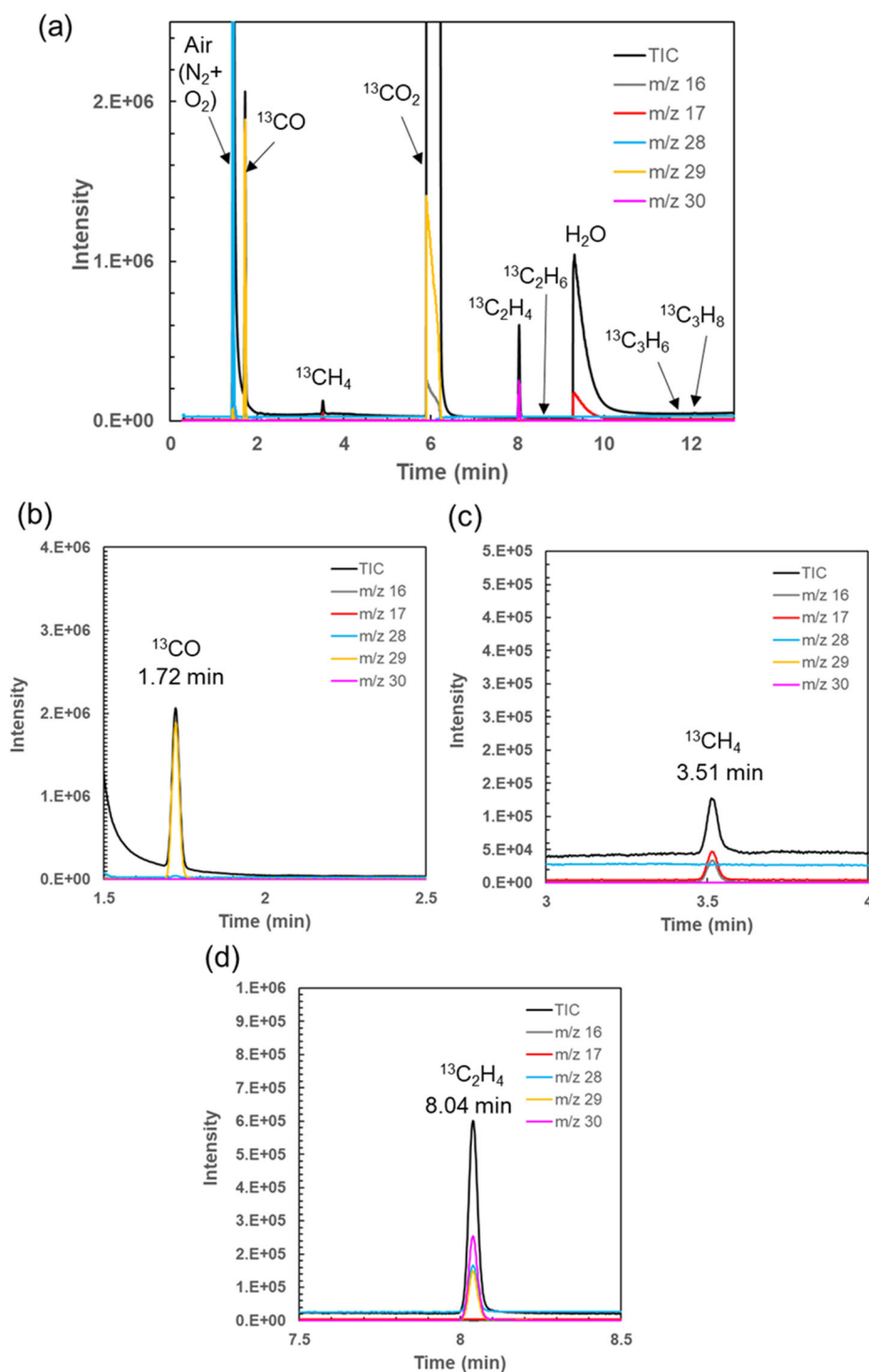


Fig.S7 Total ion current (TIC) chromatogram and extracted ion chromatogram (EIC) of gas products ¹³CO₂ electrochemical reduction over activated Cu-19 at% Ni NP/CP obtained by GC-MS (in ¹³CO₂-saturated 0.05 M KH¹³CO₃ at -1.2 V vs. RHE for 3 h): (a) overall chromatogram (retention time 0-13 min), (b) ¹³CO (1.72 min, *m/z* 29 signal), (c) ¹³CH₄ (3.51 min, *m/z* 17 signal; *m/z* 16 signal was also observed with the desorption of hydrogen from methane), and (d) ¹³C₂H₄ (8.04 min, *m/z* 30 signal; *m/z* 28 and 29 signals were also observed with the desorption of hydrogen from ethylene). For GC-MS spectra see Fig. S8.

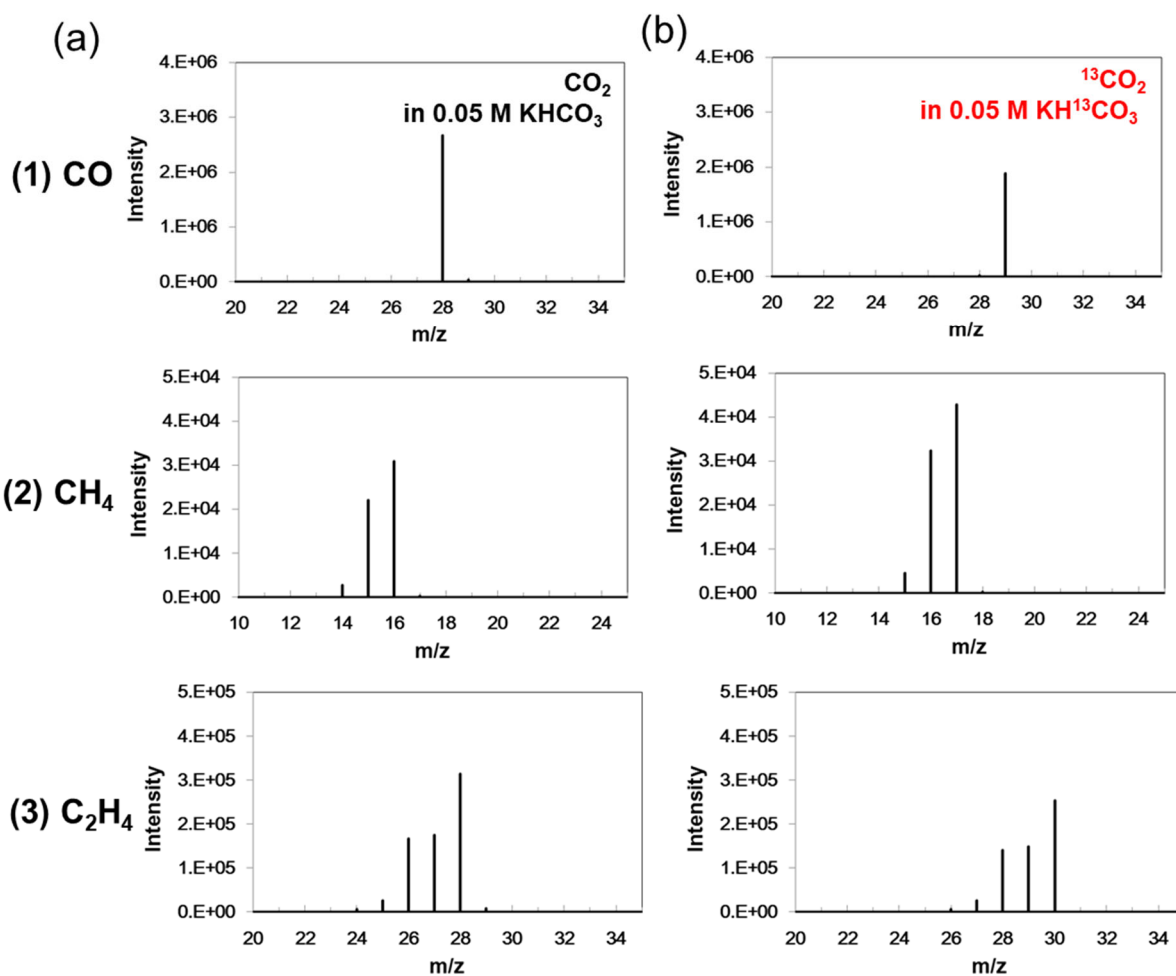


Fig. S8 GC-MS spectra of the gas products for (a) CO_2 and (b) $^{13}\text{CO}_2$ electrochemical reduction over activated Cu-19 at% Ni NP/CP in CO_2 -saturated 0.05 M KHCO_3 or $\text{KH}^{13}\text{CO}_3$ solution at -1.2 V vs. RHE for 3 h.

(1) m/z=28 and m/z=29 signals correspond to CO and $^{13}\text{CO}_2$, respectively.

(2) m/z=16 and m/z=17 signals correspond to CH_4 and $^{13}\text{CH}_4$, respectively.

Fragment ions were also observed with the desorption of hydrogen from methane.

(3) m/z=28 and m/z=30 signals correspond to C_2H_4 and $^{13}\text{C}_2\text{H}_4$, respectively.

Fragment ions were also observed with the desorption of hydrogen from ethylene.

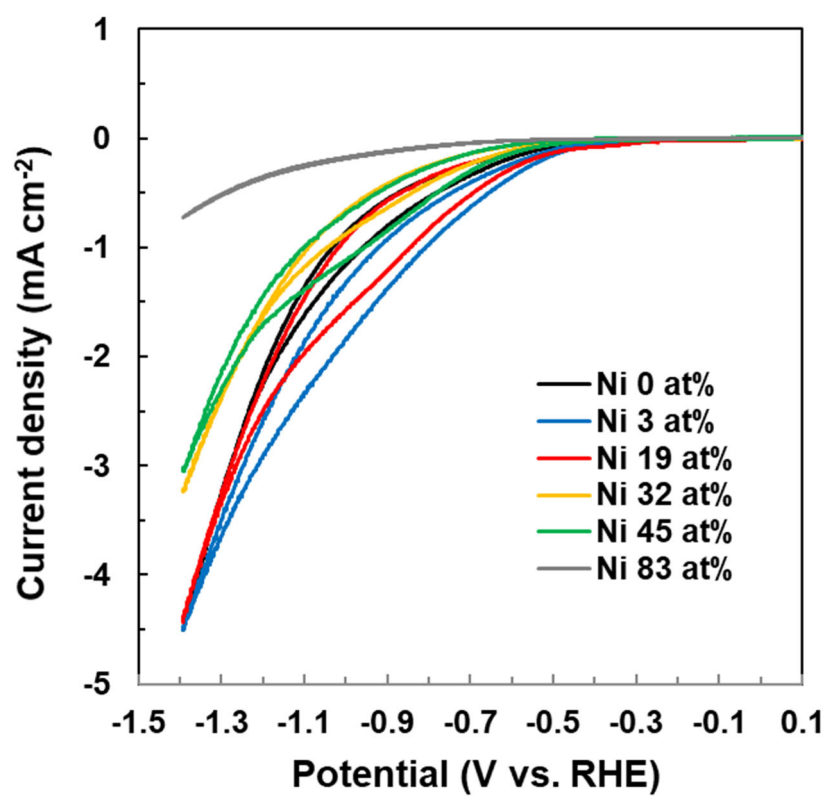


Fig. S9 Current-potential curves acquired by activated Cu-Ni NPs (Ni 0, 3, 19, 32, 45, and 83 at%) electrodes measured in CO₂-saturated 0.05 M KHCO₃ solution.

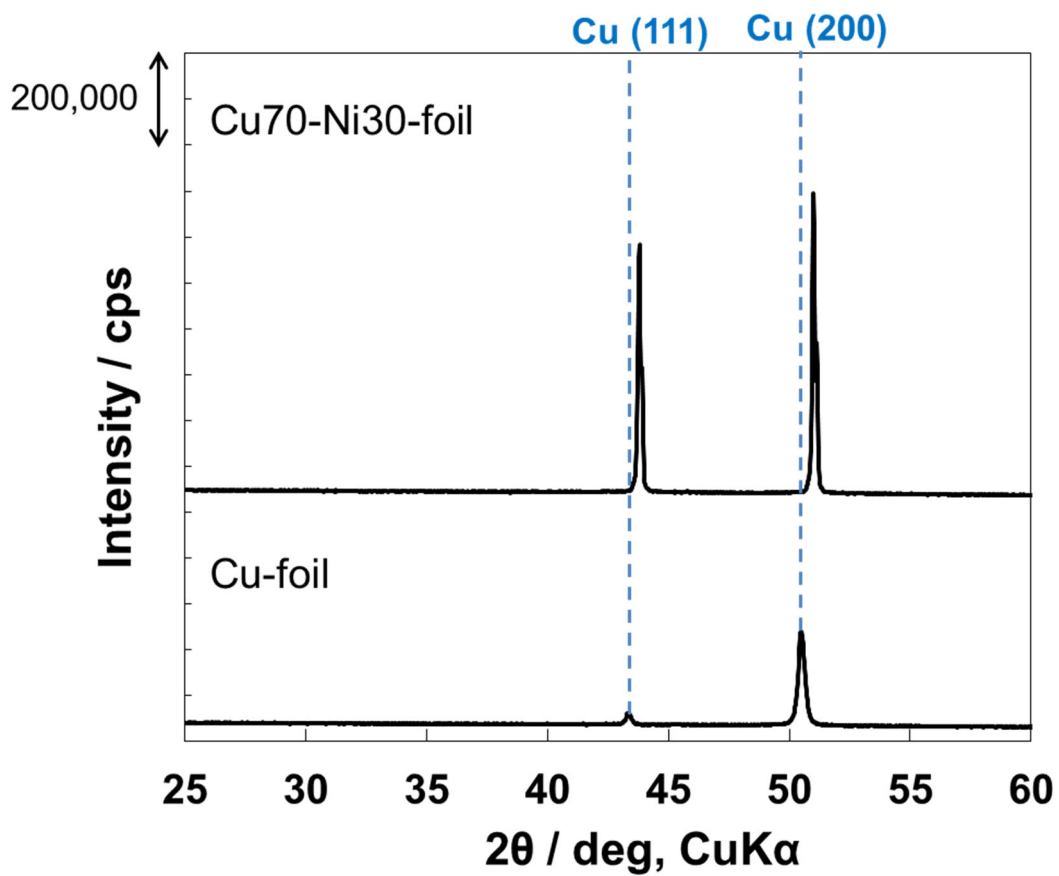


Fig. S10 XRD patterns of Cu and Cu-30 at% Ni foil.

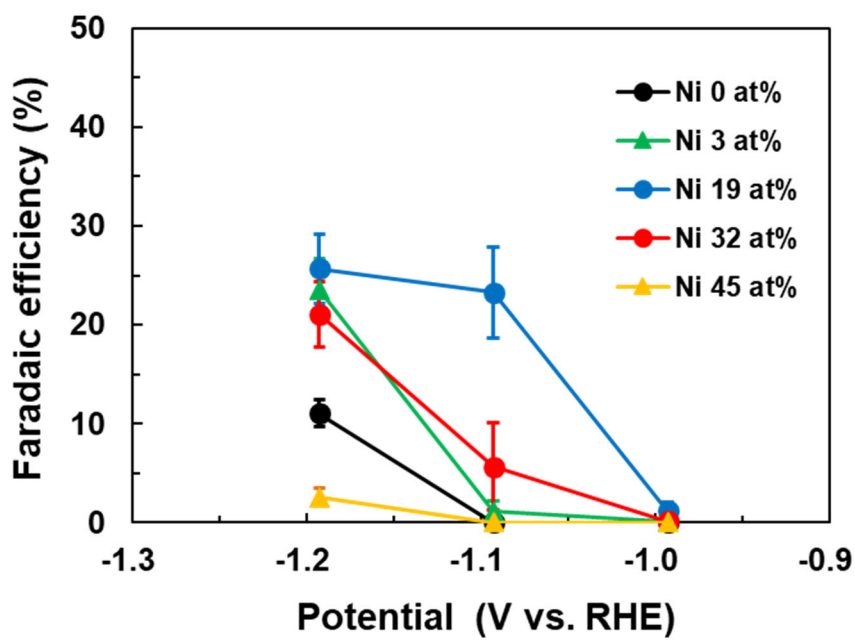


Fig. S11 Comparison of the Faradaic efficiencies for C_2H_4 production over the Cu-Ni NPs/CP electrodes in CO_2 -saturated 0.05 M $KHCO_3$ solution.

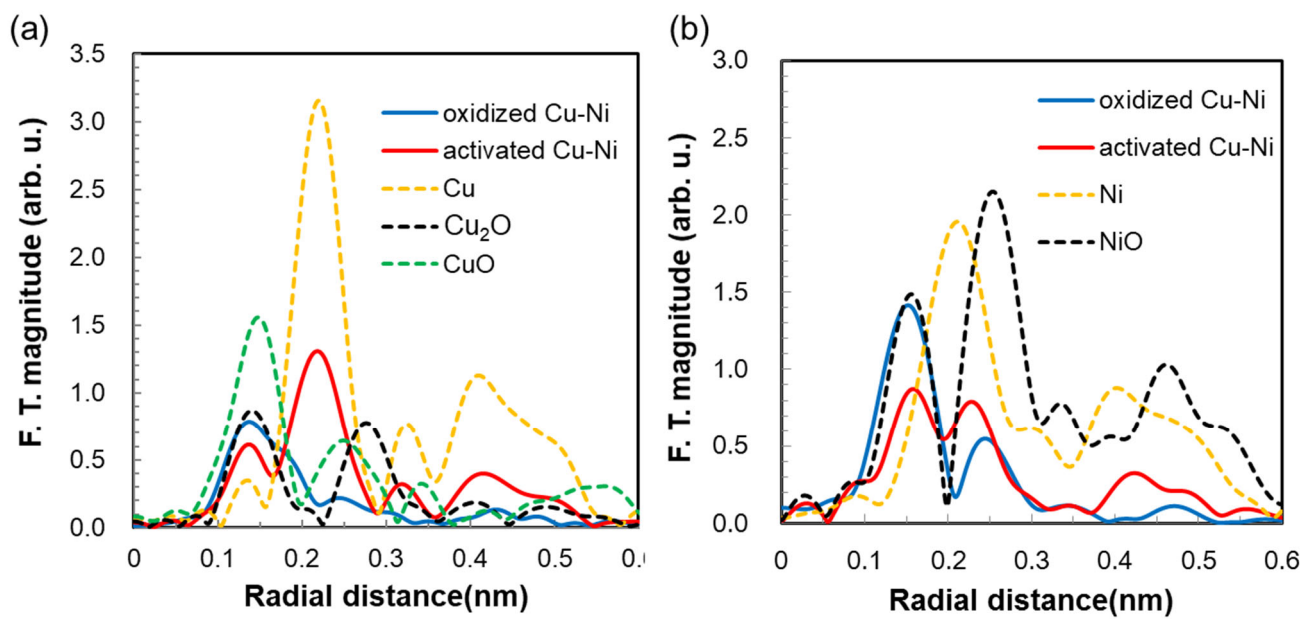


Fig. S12 k^2 -weighted FT-EXAFS (a) Cu K-edge and (b) Ni K-edge spectra for oxidized (blue line) and activated (red line) Cu-19 at% Ni NP on CP.

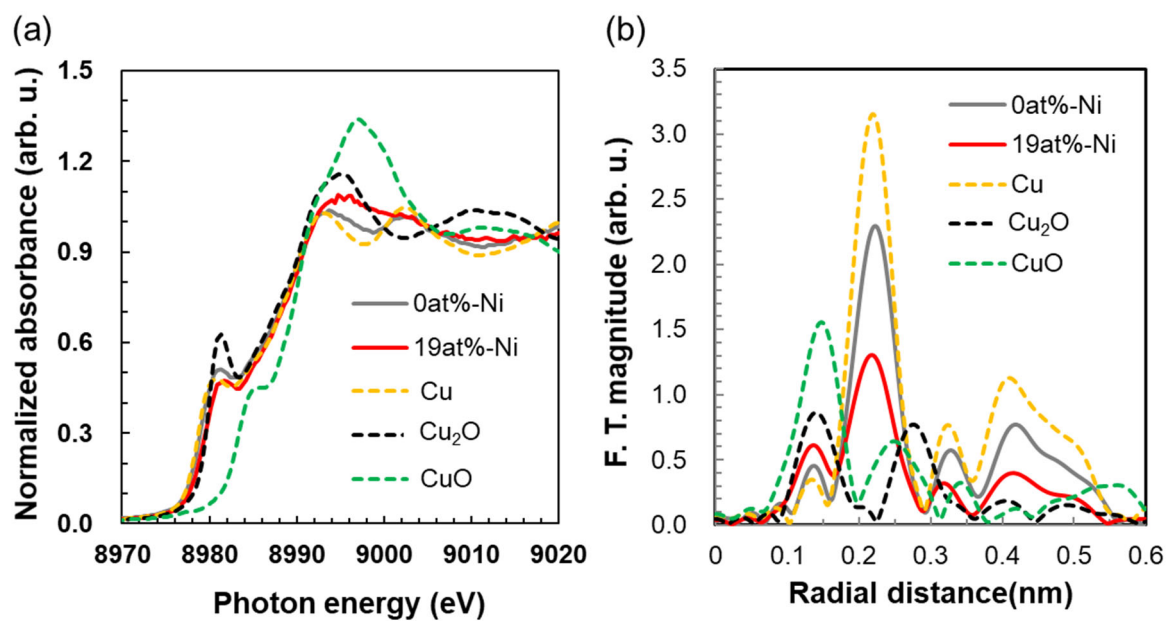


Fig. S13 Cu K-edge (a) XANES and (b) k^2 -weighted FT-EXAFS spectra of activated Cu and Cu-Ni (19 at%-Ni) NPs on CP.

Table S1 Atomic ratio evaluated from ICP data for oxidized, activated and after reaction of Cu-19 at% Ni NP on carbon paper support.

sample	Ni/(Cu+Ni) (atomic ratio, at%)
as-synthesized ^{a)}	19
oxidized	21
activated	20
after reaction (5 h) ^{b)}	18

a) See Ref. 1 data

b) Evaluation of Fig. 1(c)

References

1. R. Watanabe and T. Ishizaki, J. Mater. Chem. C, 2014, 2, 3542-3548.