Supporting Information

Selective Electrochemical Reduction of Carbon Dioxide to Ethylene on Copper Hydroxide Nitrate Nanostructure Electrode

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Reagents

Reagents including $Cu(NO_3)_2$•$3H_2O$ (99.99%), $KHCO_3$ (99.995%), D_2O (99.9 atom % deuterium), dimethyl sulfoxide (DMSO, 99.9%) were purchased from Aladdin chemical company and used without further purification. Cu mesh was purchased from Suzhou jiashide metal foam Co., Ltd. HCl and ethanol were analytical pure and purchased from SHIJIKEBO Co., Ltd. The water used in the whole experiment was ultrapure water (Sartorius-mini plus UV, 18.2 MΩ cm^{-1}). CO_2 (99.999%) and N_2 (99.999%) gases were purchased from Air Liquid Co., Ltd.

Physical and chemical characterizations

Powder X-ray diffraction (PXRD) patterns were obtained with a Rigaku SmartLab 9.0 using Cu Kα radiation (λ = 1.54056 Å), and the data were collected in Bragg-Brettano mode in the 2θ range from 5° to 80° at a scan rate of 5° min^{-1}. Scanning electron microscopic (SEM) images were captured on a FEI Nova Nano SEM 450 hot field-emission scanning electron microscope operated at an acceleration voltage of 20 kV. Transmission electron microscopy (TEM) images were collected on a FEI Tecnai G2 F30 S-TWIN transmission electron microscope with an acceleration voltage of 300 kV. X-ray photoelectron spectroscopy (XPS) spectra were taken on a ThermoFisher ESCALAB^{TM} 250Xi surface analysis system using a monochromatized Al Kα small-spot source, and the corresponding BEs were calibrated by referencing the C 1s to 284.8 eV.

Electrochemical measurements

All electrochemical measurements were run in a customized gastight two-compartment electrochemical cell using a three-electrode configuration with 85% iR correction. Typically, the $Cu@Cu_2(OH)_3NO_3$ electrode (0.5*0.5 cm^2) after pre-reduction was used as work electrode, a leakless Ag/AgCl electrode (Saturated KCl, Tjaida) as the reference electrode, and the two were mounted in the cathodic compartments. The $Ti@IrO_2$ was used as the counter electrode and mounted in the anodic compartments. An anion-exchange membrane (Selemion AMVN, AGC Inc.) was used to separate the cathodic and anodic compartments to eliminate the oxidation of the liquid products at the anode surface. The volumes of catholyte and anolyte were 10 mL and 7 mL respectively. The headspace of the cathodic compartment was about 6 mL. 0.1 M $KHCO_3$ aqueous solution was used as the electrolyte and it was pre-saturated with high-purity CO_2. The resulted pH after saturation was 6.8. CO_2 gas was flowed into catholyte at a flow rate of 10 Standard Cubic Centimeters per Minute (SCCM) during the reaction, and the electrolyte was stirred by a stir bar during the electrolysis. The cell was connected to the potentiostat (Autolab) and chronoamperometry (CA) experiments were performed for 40 minutes at different potentials to measure the FE of different products. The gas products were detected using a gas chromatograph (GC, Thermo Fisher) equipped with a thermal conductivity detector (TCD) for hydrogen (H_2) and two flame ionization detectors (FID) for CO, methane (CH_4), ethane (C_2H_6) and ethylene (C_2H_4). The identification of gaseous products was based on the retention time. The amount of gaseous products was calculated based on the peak areas. The peak identification and peak area were calibrated using standard calibration gas with known concentration of H_2, CO, CH_4, C_2H_6 and C_2H_4 mixed with Ar from a commercial supplier (Dalian GuangMing Special Gas Products Co., Ltd.). The liquid products were quantified using ^1H NMR spectra (^1H NMR, 400 MHz, Bruker) with a water suppression technique. Typically, 2 mL of D_2O and 10 μL DMSO was mixed firstly. Then, 100 μL of the above mixed solution was added into 600 μL of catholyte after electrolysis in a 5 mm NMR glass tube, where the D_2O and DMSO were the lock field reagent and internal standard respectively. The area ratios of the products to DMSO were compared to the standard calibration curves to quantify the concentration of different liquid products. The Potential (E) was converted to the RHE reference electrode using the following equation:

$$E\ (vs.\ \mathrm{RHE}) = E\ (vs.\ \mathrm{Ag/AgCl}) + 0.1976 + 0.059*\mathrm{pH}$$

Solution resistance (Rs) was determined by potentiostatic electrochemical impedance spectroscopy (PEIS) at frequencies ranging from 10^5 Hz to 1 Hz and an AC amplitude of 5 mV was applied.

Pre-reduction of $Cu@Cu_2(OH)_3NO_3$

The as prepared $Cu@Cu_2(OH)_3NO_3$ electrode was cut into bars with the dimension of $2*0.5\ cm^2$. The electrode was pre-reduced at $-20\ mA/cm^2$ in CO_2-saturated 0.1 M $KHCO_3$. The pre-reduction time was 20 minutes. The color of the electrode became reddish after the prereduction.

Preparation of $Ti@IrO_2$ electrode

$Ti@IrO_2$ electrode was prepared according to previous literature with slight modifications[1]. Titanium foil (2*1*0.25 cm) was etched in boiling 1 M oxalic acid solution for 40 min, dried with a N_2 flow after rinsing with abundant water. Subsequently, 50 μL of 0.2 M H_2IrCl_6 in isopropanol was drop cast on one side of the foil. After drying at 70°C for 10 min, the other side of foil was treated with the same process. Then, the foil was calcined at 500 °C for 10 min in air. The above process was repeated three times, finally the $Ti@IrO_2$ electrode was obtained.

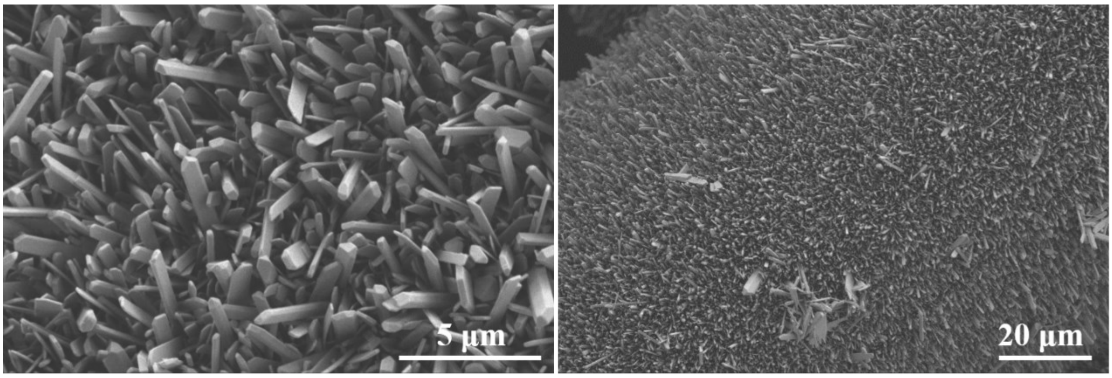
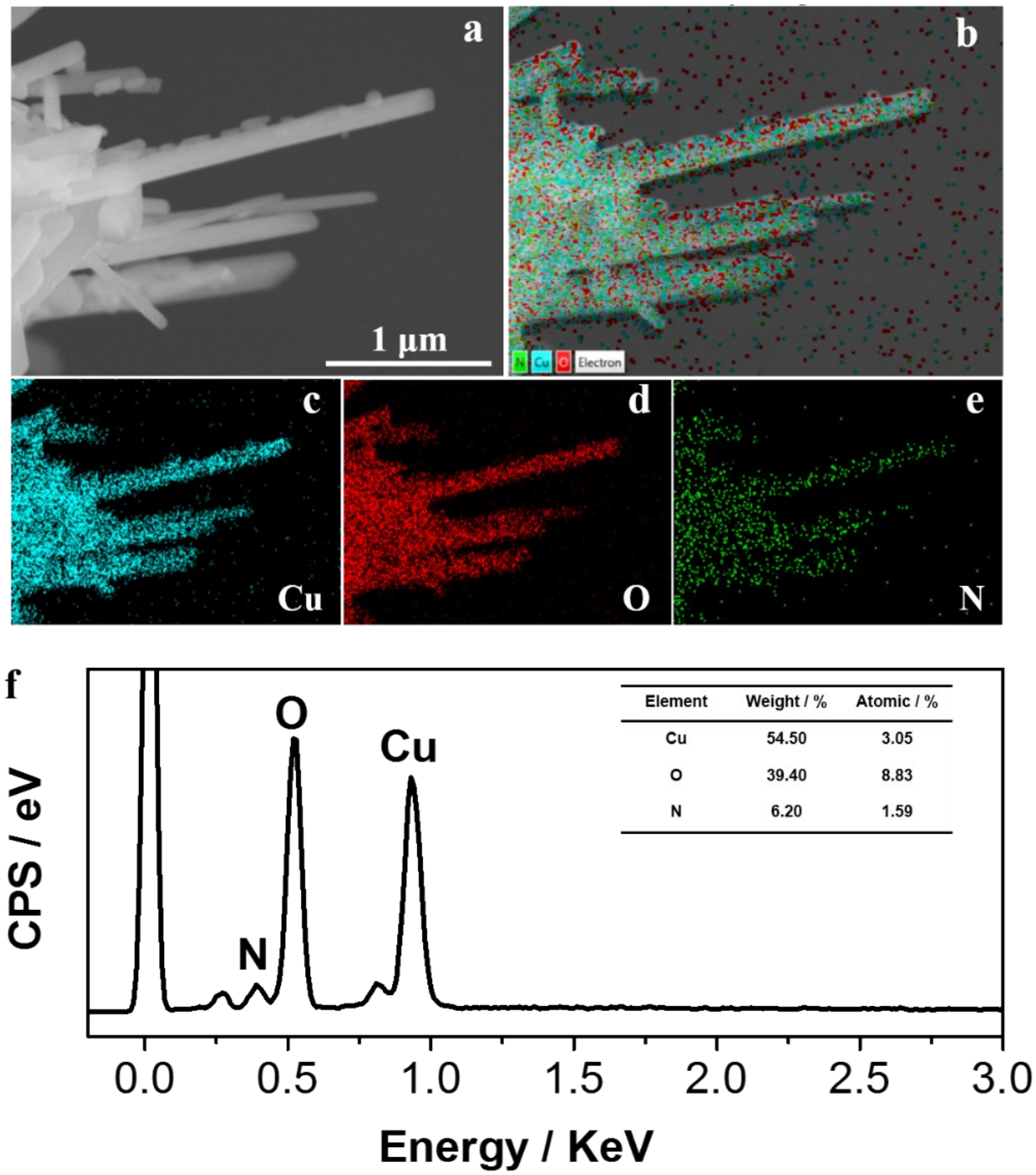


Figure S1. SEM images of the pristine Cu@$Cu_2(OH)_3NO_3$ electrode.



Element	Weight / %	Atomic / %
Cu	54.50	3.05
O	39.40	8.83
N	6.20	1.59

Figure S2. SEM images (a) and the corresponding elemental mapping images of (b) mixed, (c) Cu, (d) O, (e) N of the pristine Cu@$Cu_2(OH)_3NO_3$ electrode, (f) energy dispersive X-ray spectroscopy of the pristine Cu@$Cu_2(OH)_3NO_3$ electrode.

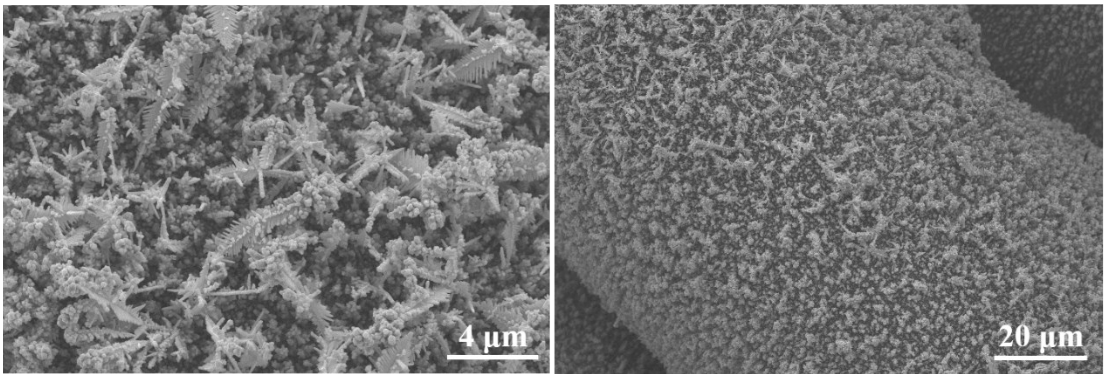
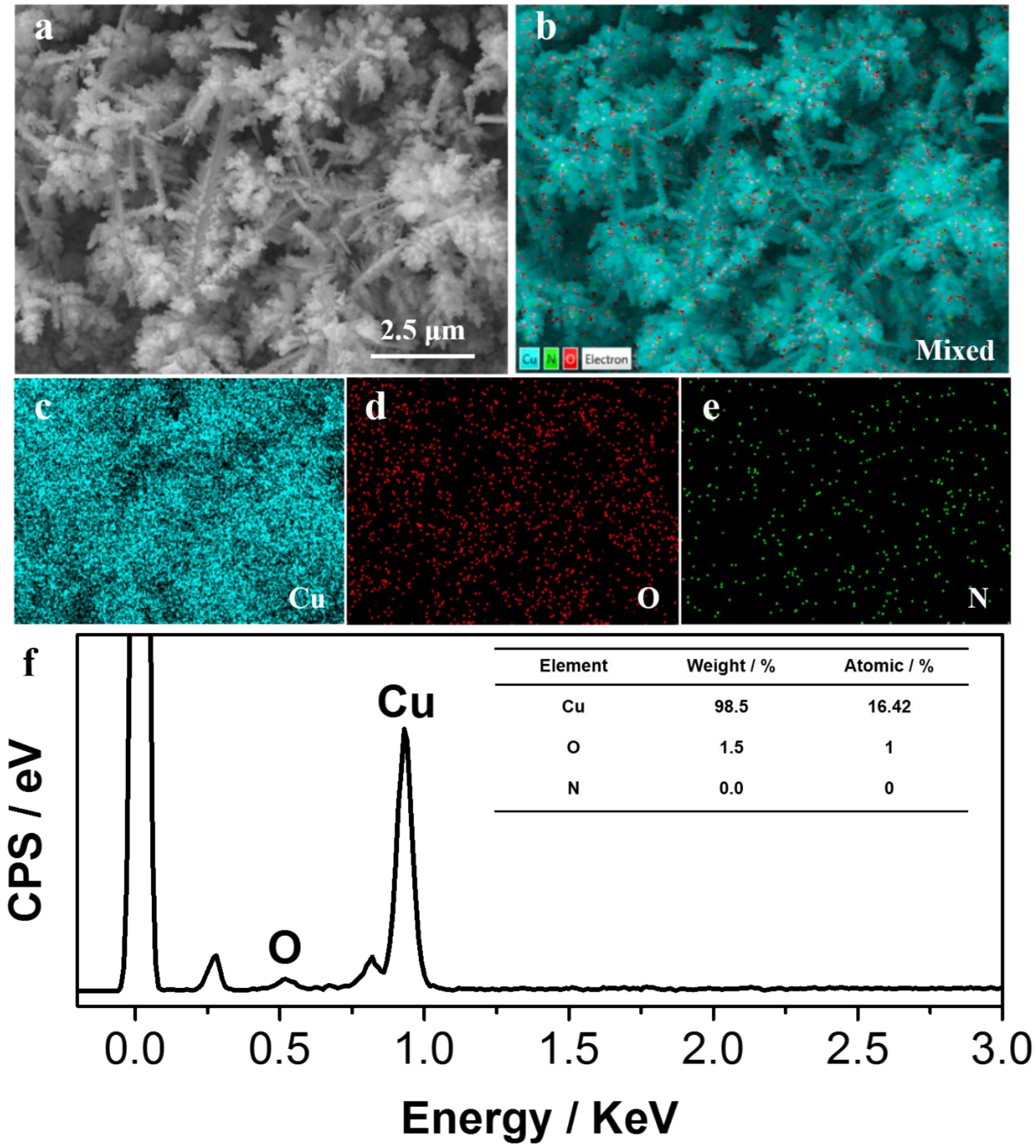


Figure S3. (a) SEM images of the Re-Cu@$Cu_2(OH)_3NO_3$ electrode.



Element	Weight / %	Atomic / %
Cu	98.5	16.42
O	1.5	1
N	0.0	0

Figure S4. (a) SEM images and corresponding elemental mappings (b-e), and (f) The EDS pattern of the Re-Cu@$Cu_2(OH)_3NO_3$ electrode.

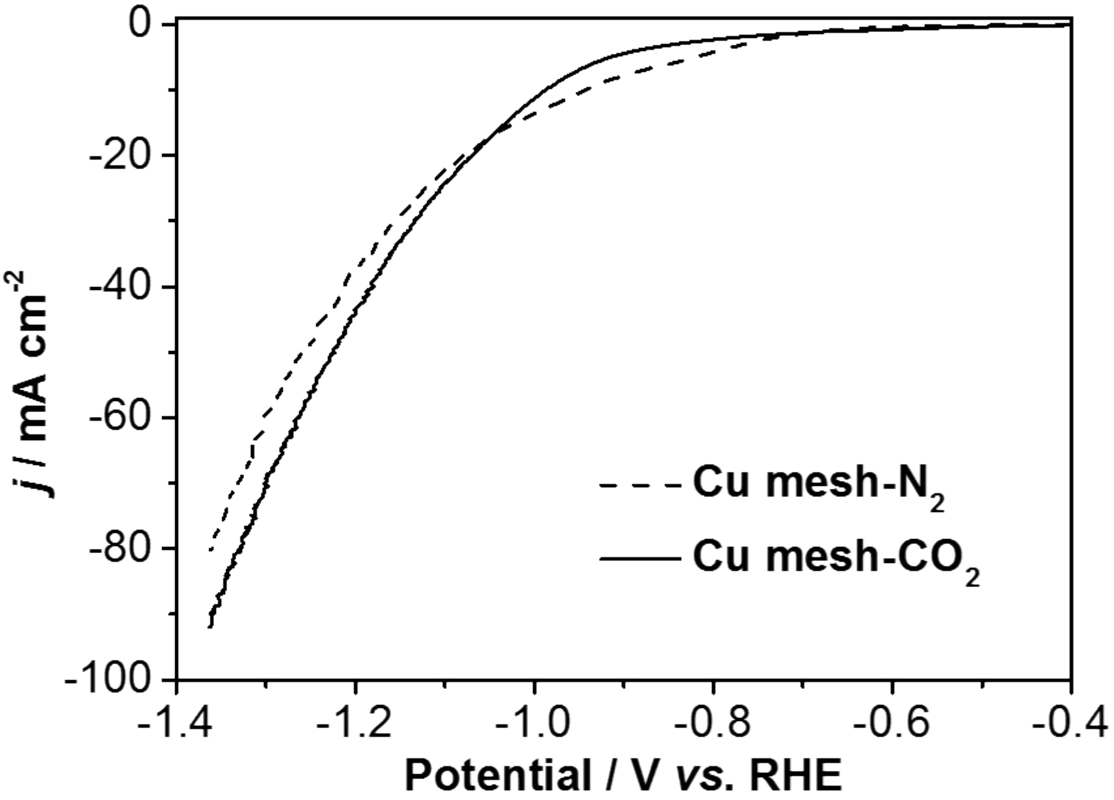


Figure S5. LSV curves of the Cu mesh electrode in Ar (dashed) and CO_2 (solid) saturated 0.1 M $KHCO_3$ solution, without stir, scan rate, 20 mVs^{-1}.

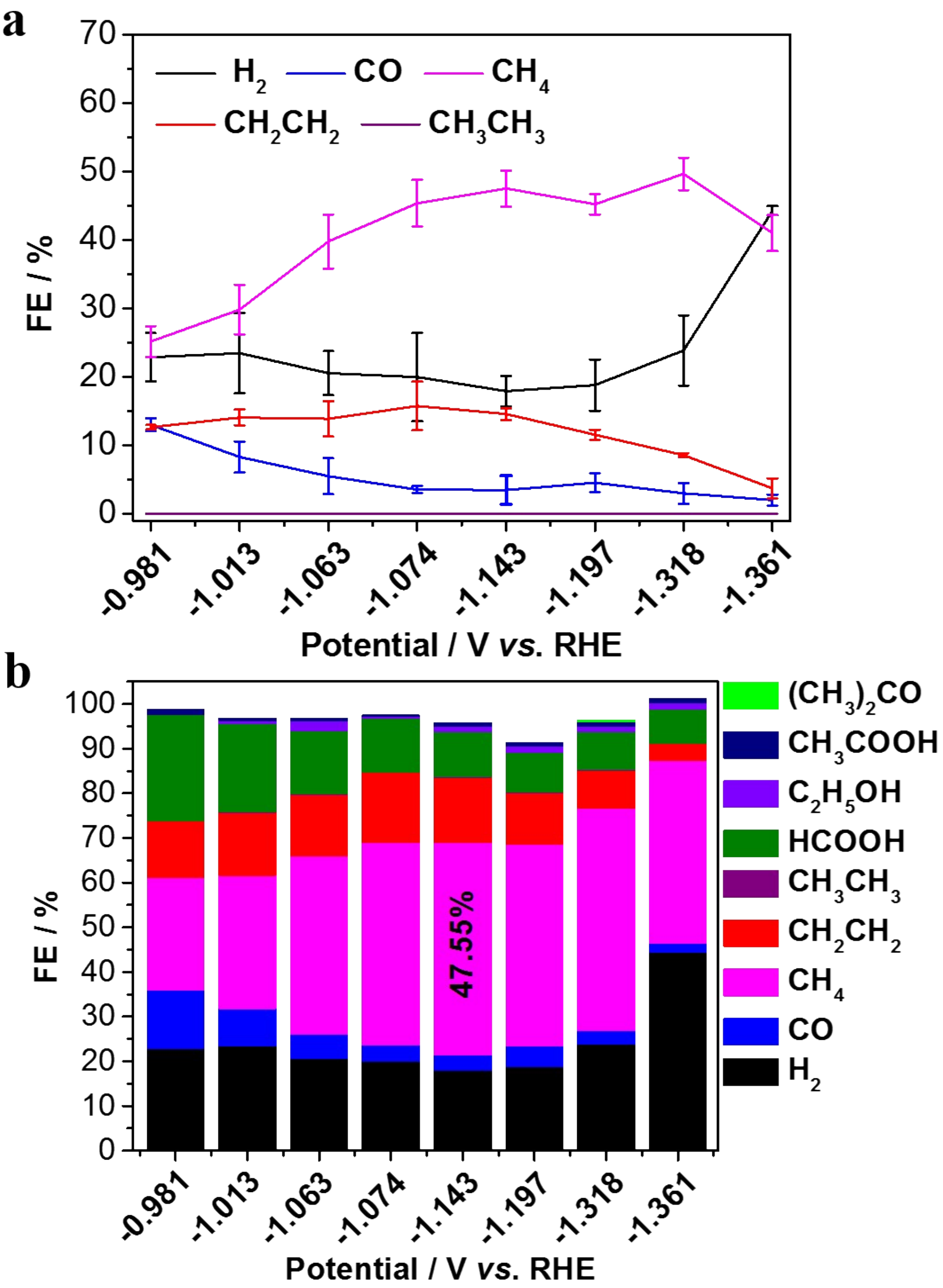


Figure S6. Faradaic efficiency of the (a) gaseous and the (b) total detectable products as a function of applied potentials on Cu mesh electrode.

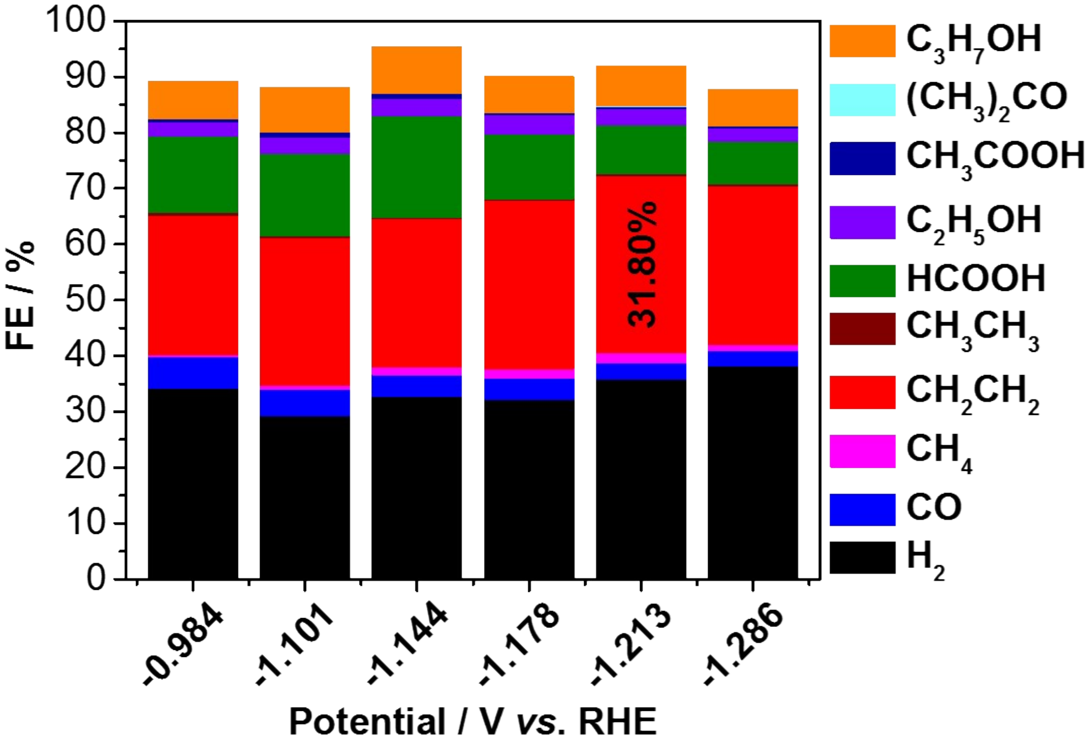


Figure S7. Faradaic efficiency of the total detectable products as a function of applied potentials on the Re-Cu@$Cu_2(OH)_3NO_3$ electrode.

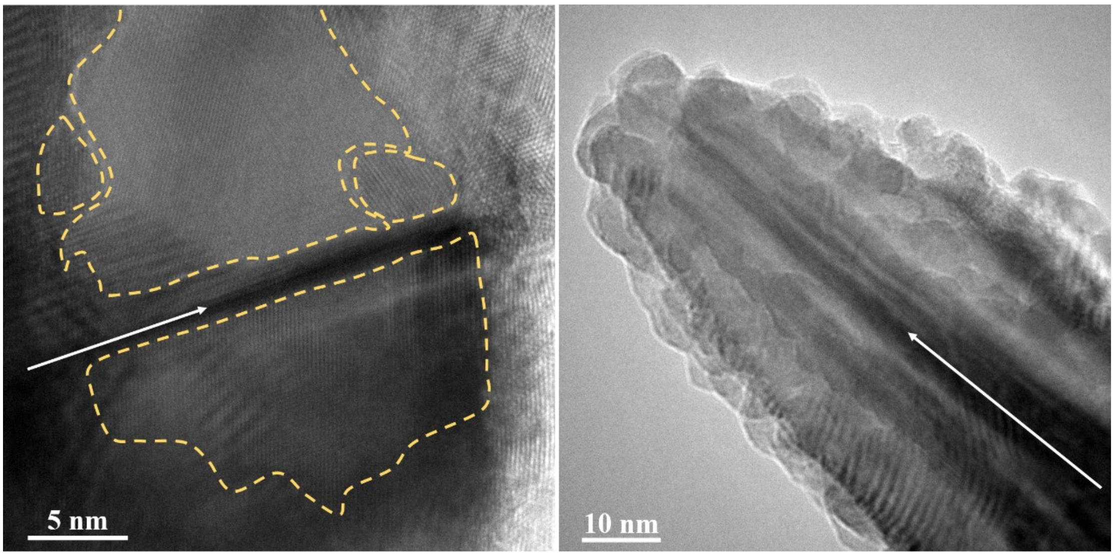


Figure S8. HRTEM images of Re-Cu@$Cu_2(OH)_3NO_3$ nanodendrites, The arrows indicate the gain boundaries.

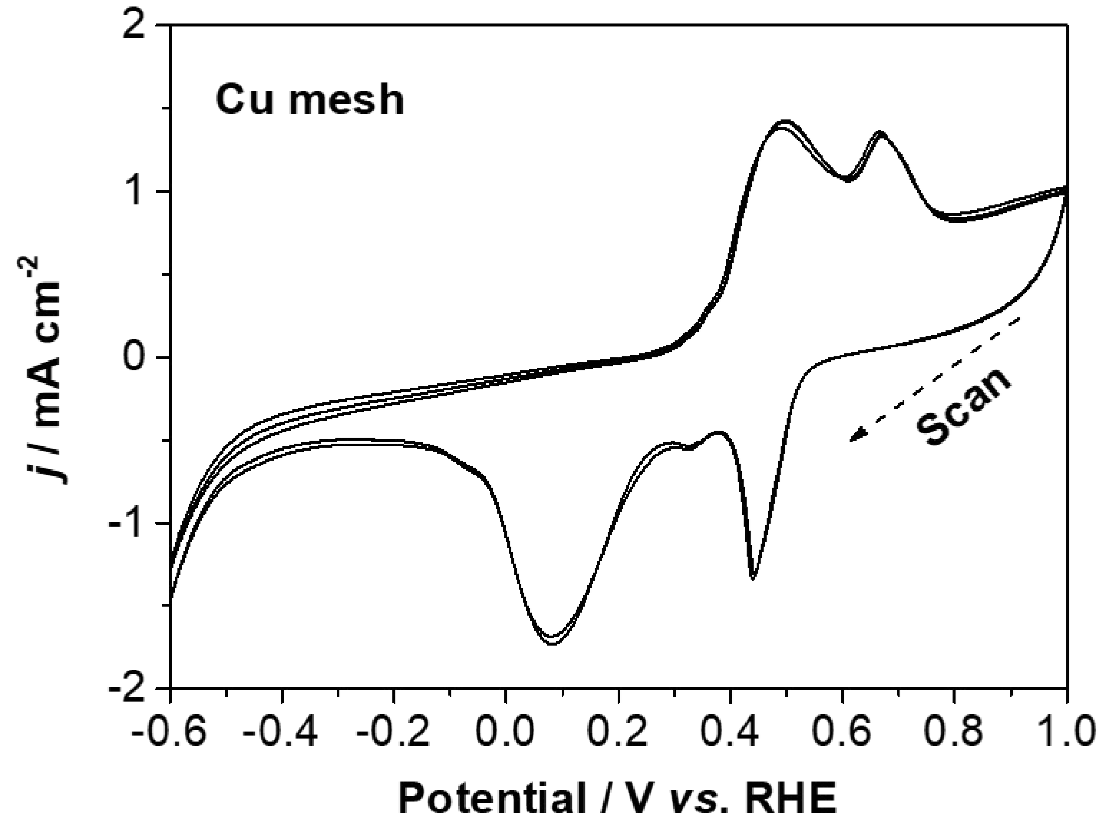


Figure S9. Enlarged cyclic voltammograms of the bare Cu mesh electrodes in 0.1 M $KHCO_3$ (saturated with Ar), without stir, scan rate: 20 mV/s.

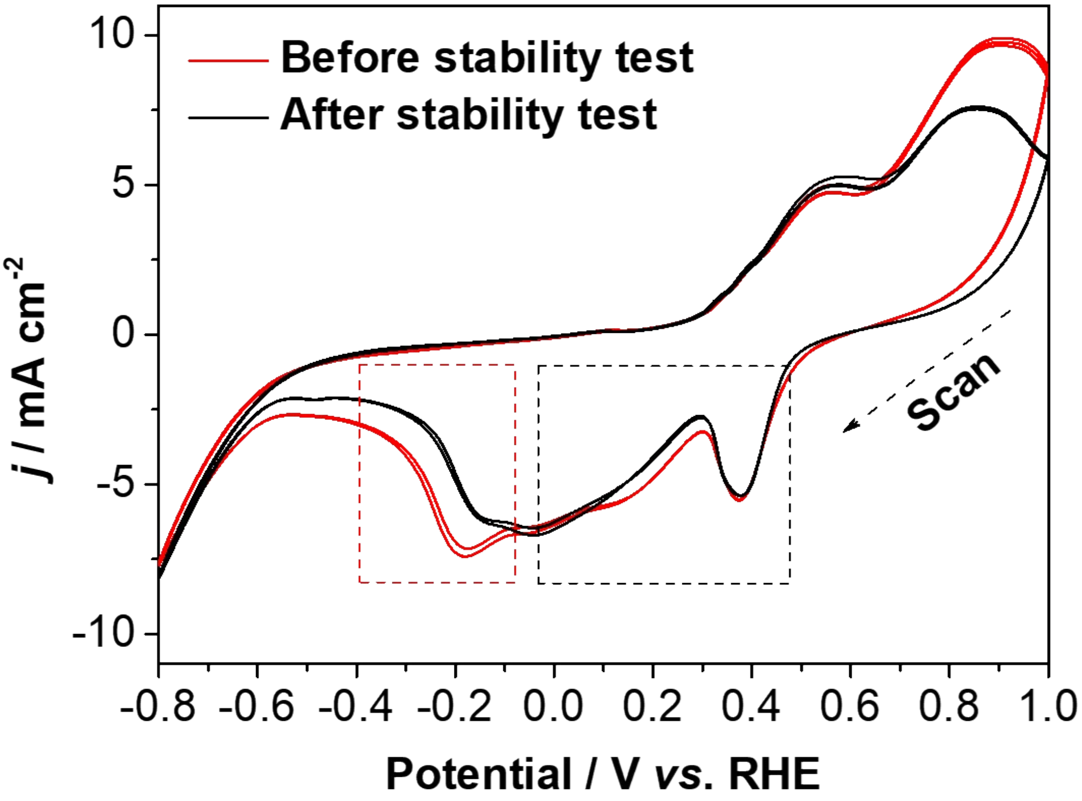


Figure S10. Cyclic voltammograms of the Re-Cu@$Cu_2(OH)_3NO_3$ electrode before and after 20 h continuous electrolysis at -1.213 V (*vs.* RHE) for 4 segments respectively. Electrolyte, 0.1 M $KHCO_3$ (saturated with Ar), without stir, scan rate: 20 mV/s.

Table S1. Faradaic efficiency of all detectable products on Cu mesh electrode at different applied potentials.

E *vs.* RHE (V)	**H_2**	**CO**	**CH_4**	**C_2H_4**	**C_2H_6**	**$HCOO^-$**	**C_2H_5OH**	**CH_3COO^-**	**C_3H_7OH**
-0.981	22.88	13.02	25.20	12.66	0.06	23.90	/	1.10	/
-1.013	23.48	8.31	29.85	14.09	0.06	19.80	0.70	0.60	/
-1.063	20.56	5.52	39.80	13.90	0.04	14.10	2.20	0.70	/
-1.074	20.00	3.56	45.39	15.77	0.03	12.00	0.40	0.40	/
-1.143	17.95	3.50	47.55	14.60	0.03	10.20	1.10	0.90	/
-1.197	18.82	4.56	45.24	11.57	0.05	8.90	1.40	0.80	/
-1.318	23.90	3.02	49.68	8.59	0.04	8.50	1.30	0.90	0.50
-1.361	44.31	2.04	41.03	3.73	0.05	7.70	1.40	0.90	/

Each data present here are an average of at least 3 parallel tests;

/: not detectable

Table S2. Faradaic efficiency of all detectable products on Re-Cu@$Cu_2(OH)_3NO_3$ electrode at different applied potentials.

E *vs.* RHE	**H_2**	**CO**	**CH_4**	**C_2H_4**	**C_2H_6**	**$HCOO^-$**	**C_2H_5OH**	**CH_3COO^-**	**$(CH_3)_2CO$**	**C_3H_7OH**
-0.984	34.15	5.71	0.36	24.87	0.56	13.70	2.60	0.60	/	6.60
-1.101	29.27	4.74	0.77	26.34	0.43	14.80	2.90	0.80	/	8.10
-1.144	32.69	3.94	1.34	26.55	0.27	18.20	3.10	0.90	/	8.50
-1.178	32.23	3.76	1.75	30.08	0.34	11.50	3.50	0.40	/	6.50
-1.213	35.82	2.98	1.70	31.80	0.36	8.70	2.90	0.40	0.10	7.15
-1.286	38.18	2.71	1.12	28.37	0.36	7.70	2.40	0.40	/	6.50

Each data present here are an average of at least 3 parallel tests;

/: not detectable

Table S3. Summary of the peaks area of the fitted O XPS spectra of the pristine Cu@$Cu_2(OH)_3NO_3$ and Re-Cu@$Cu_2(OH)_3NO_3$ electrodes.

Electrode	**Bond**	**Peak area**
pristine Cu@$Cu_2(OH)_3NO_3$	O-H	29184.87
	O-Cu	18362.32
Re-Cu@$Cu_2(OH)_3NO_3$	O-H	25576.8
	O-Cu	8692.46

References

[1] M. Schreier, L. Curvat, F. Giordano, L. Steier, A. Abate, S. M. Zakeeruddin, J. Luo, M. T. Mayer and M. Grätzel, Nat. Commun. 2015, 6, 7326-7332.