

Supplementary Information

**Synergy of Cu-Doping and *In situ* Reconstruction on Bi₂O₂CO₃ for Promoting
CO₂ Electroreduction Over Wide pH Range**

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Experimental Section

Chemicals and materials.

Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\geq 99.0\%$), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\geq 99.0\%$), acetic acid ($\text{C}_2\text{H}_4\text{O}_2$, $\geq 99.5\%$), ammonium hydroxide aqueous solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25.0% ~ 28.0%), ethanol, potassium hydroxide (KOH , $\geq 99.5\%$), potassium sulfate (K_2SO_4 , $\geq 99.0\%$), sulfuric acid (H_2SO_4 , 95.0% ~ 98.0%), and dimethyl sulfoxide (DMSO, $\geq 99.8\%$) were purchased from Sinopharm Chemical Co., Ltd. Potassium bicarbonate (KHCO_3 , $\geq 99.5\%$) was purchased from Macklin. Deuterioxide (D_2O , $\geq 99.8\%$) was purchased from Energy Chemical Co., Ltd. Carbon papers (YLS-30T, SGL 29BC) and Nafion (Dupont, D520) were purchased from Suzhou Sinero Technology Co., Ltd. All chemicals were of analytical grade and used without further purification. All the aqueous solutions were prepared with ultrapure deionized water ($18.25 \text{ M}\Omega \cdot \text{cm}$) through a Millipore system.

Preparation of BOC

$\text{Bi}_2\text{O}_2\text{CO}_3$ (BOC) catalyst was prepared by a one-step hydrothermal reaction method. Specifically, 2.0 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in a mixture containing 4 mL deionized water (DI), 2 mL acetic acid, and 12 mL ammonia water. After stirring for 30 minutes at room temperature, the homogeneous precursor solution was transferred to a 50 mL PTFE-lined autoclave and kept at 180 °C for 12 hours. After cooled to room temperature, the solution was centrifuged by repeatedly washing with DI, and then dried in a vacuum oven at 60 °C for 24 hours.

Preparation of Cu-doped BOC

The synthesis procedure of Cu-doped BOC is similar to that of BOC, except for adding 2.0 mmol $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ into the precursor solution.

Material characterizations.

X-ray diffraction (XRD) patterns of the samples were collected on X-ray diffractometer (Smart Lab 3KW) with Cu-K α radiation ($\lambda=1.5418 \text{ \AA}$) operating at 36 kV and 30 mA. The morphology and size of samples were investigated by scanning electron microscopy (SEM, Carl Zeiss, Sigma 500) and transmission electron

microscopy (TEM, FEI, Talos F200X) equipped with EDS (Super-X). HAADF-STEM images were recorded on a Thermo Fisher Scientific TEM (Themis Z) working at 300 kV. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250xi) was equipped with Al K α as an exciting X-ray source, in which the binding energies were corrected referring to the binding energy of the C 1s peak at 284.8 eV. The *ex situ* Raman spectrum was collected on Microscopical Laser Raman spectroscopy (Thermofisher DXR2).

Electrochemical measurements.

CO₂RR measurements in H-cell:

Electrochemical measurements were conducted in an air-tight H-cell (Gaoss Union) on an electrochemical workstation (CHI 660E). The two compartments of the three-electrode H-cell, filled with 50 mL 0.5 M KHCO₃ electrolyte each, are separated by a Nafion-117 membrane. The working electrode and Ag/AgCl (KCl-saturated) reference electrode were in the cathodic compartment, and Pt plate as counter electrode was in the anodic compartment. Before electrochemical test, the electrolyte was bubbled with CO₂ gas for at least 20 minutes. The working electrode was prepared by loading the electrocatalyst on the carbon papers (YLS 30T, 1 × 1 cm² or GDS 2230, 2 × 2 cm²). During the electrochemical test, the electrolyte was continuously bubbled with CO₂ gas with a flow rate of 20 sccm. All the potentials in H-cell vs. Ag/AgCl were converted to the reversible hydrogen electrode (RHE) by the equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \times \text{pH} + 0.197$$

Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were measured in 0.5 M KHCO₃ electrolyte saturated with CO₂. LSV curves were obtained at a scan rate of 10 mV s⁻¹ without iR compensation. Electrochemical impedance spectroscopy (EIS) measurements were performed at the open circuit voltage within the frequency range between 0.01 Hz and 1 × 10⁵ Hz in CO₂-saturated 0.5 M KHCO₃ electrolyte, with an AC amplitude of 5 mV. The double-layer capacitance (C_{dl}) of the catalysts was calculated by testing capacitive current density via cyclic voltammetry (CV) curves in the non-Faraday range with different scan rates in CO₂-saturated 0.5 M KHCO₃ electrolyte. The applied potentials of the collected CV curves were from -0.15 V to -0.05 V vs.

Ag/AgCl. The scan rates were 20, 40, 60, 80, and 100 mV s⁻¹, respectively. By plotting the data of $\Delta J = (J_a - J_c)$ at -0.1 V vs. Ag/AgCl against the scan rate (where J_a and J_c were the anodic and cathodic current density, respectively), the C_{dl} was half of the linear fitting slope. The Tafel slope was calculated to analyze the electrochemical reaction kinetics of CO₂RR by the following equation:

$$\eta = b \lg (j_{\text{HCOO}^-})$$

Where b is the Tafel slope (mV dec⁻¹), j_{HCOO^-} is the partial current density of HCOO⁻ (mA cm⁻²), η is the overpotential difference between the standard CO₂/HCOO⁻ reduction potential E_0 and the applied potential.

CO₂RR measurements in flow cell:

The catholyte and anolyte chambers of the flow cell were separated by a anion exchange membrane (Fumasep FAA-3-PK 130). When applying 1 M KOH, 0.5 M KHCO₃ and 0.5 M K₂SO₄ + H₂SO₄ (pH=2) as the electrolytes, Hg/HgO electrode, Ag/AgCl (KCl-saturated) electrode and Hg/Hg₂SO₄ electrode were selected as the corresponding reference electrodes, respectively. Pt foil (1 × 1 cm²) was used as the counter electrode. The potentials in flow cell vs. Hg/HgO and vs. Hg/ Hg₂SO₄ were converted to the reversible hydrogen electrode (RHE) by the equation:

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.0591 \times \text{pH} + 0.098$$

$$E_{\text{RHE}} = E_{\text{Hg/Hg}_2\text{SO}_4} + 0.0591 \times \text{pH} + 0.65$$

During CO₂RR test, 0.5 M KHCO₃, 1 M KOH and 0.5 M K₂SO₄ + H₂SO₄ (pH=2) were used as the electrolyte circulated at 15 mL min⁻¹ and CO₂ was directly supplied to the cathodic GDE (20 mL min⁻¹).

Quantitative analysis of gaseous and liquid products.

The gaseous products of CO₂RR were qualitatively and quantitatively assessed with an online gas chromatography (Hope, GC-9860-5C-NJ). The faradaic efficiency (FE) for gas products (H₂ or CO) was calculated as follows:

$$\text{FE}_{\text{gas}} = V_i \times \text{flow rate} \times \frac{n\text{FP}_0}{iT_0R}$$

Where V_i is the volume concentration of H₂ or CO based on a calibration of the GC, n is the number of transferred electrons for certain product ($n=2$ for H₂ and CO), F

is the Faraday constant (96500 C mol^{-1}), P_0 is the atmospheric pressure (101325 Pa), R is the molar gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T_0 is the temperature (298.15 K), i is the total current measured by an electrochemical workstation.

The liquid products were determined by an offline nuclear magnetic resonance spectrometer (JNM-ECZ600R/S1).

Preparation of NMR sample:

0.5 mL catholyte was mixed with 0.1 mL D_2O and DMSO solution (0.42 μL of DMSO, 99.58 μL of H_2O) in the NMR tube. Sonicate the mixture for 5 minutes to form a homogeneous solution.

The faradic efficiency (FE) for HCOO^- was calculated as follows:

$$\text{FE}_{\text{HCOO}^-} = V \times C \times \frac{nF}{Q}$$

V is the volume of the electrolyte in the cathode compartment, C is the concentration of HCOO^- after electrolysis determined by $^1\text{H-NMR}$, n is the number of transferred electrons for certain product ($n=2$ for HCOOH), F is the Faraday constant (96500 C mol^{-1}), Q is total charge consumed in the electrolysis.

***In situ* Raman measurements.**

In situ Raman measurements were performed using a Raman instrument (Renishaw, In Via). A Raman laser with 455 nm wavelength was utilized as the excitation source. The catalyst loaded on a silicon substrate served as working electrode, an Ag/AgCl (KCl -saturated) electrode and Pt wire were used as the reference electrode and counter electrode, respectively. A CO_2 -saturated 0.5 M KHCO_3 aqueous solution was used as the electrolyte and circulated by peristaltic pumps at a rate of 10 mL min^{-1} . Baseline correction was applied in all *in situ* Raman spectra.

***In situ* ATR-SEIRAS measurements.**

Attenuated total reflectance-surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) measurements were conducted on a Nicolet iS50 FTIR spectrometer equipped with a mercury cadmium telluride (MCT) detector and a reflectance unit for the electrochemical cell at an incidence angle of 60° .

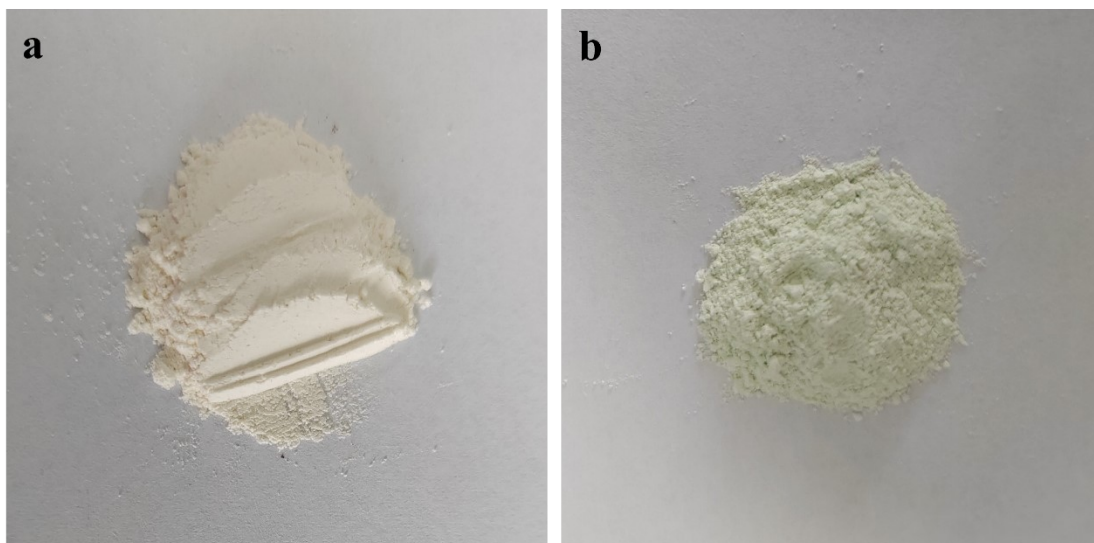


Figure S1. Pictures of (a) BOC and (b) Cu-doped BOC catalysts.

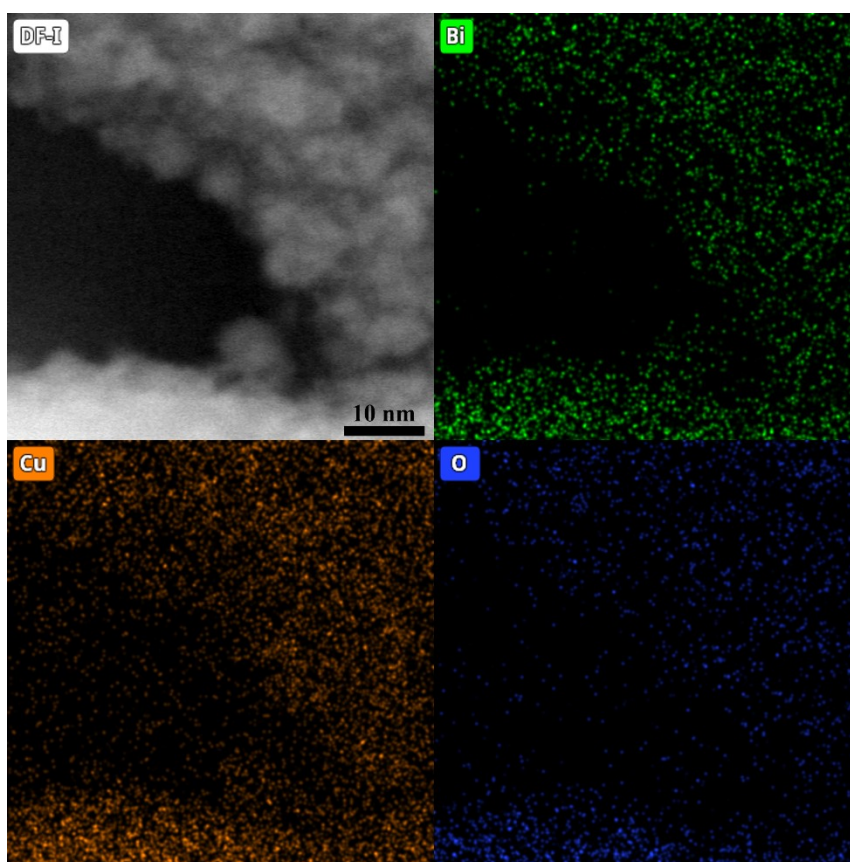


Figure S2. HAADF-STEM image of Cu-doped BOC and the corresponding elemental mappings for Bi, Cu and O.

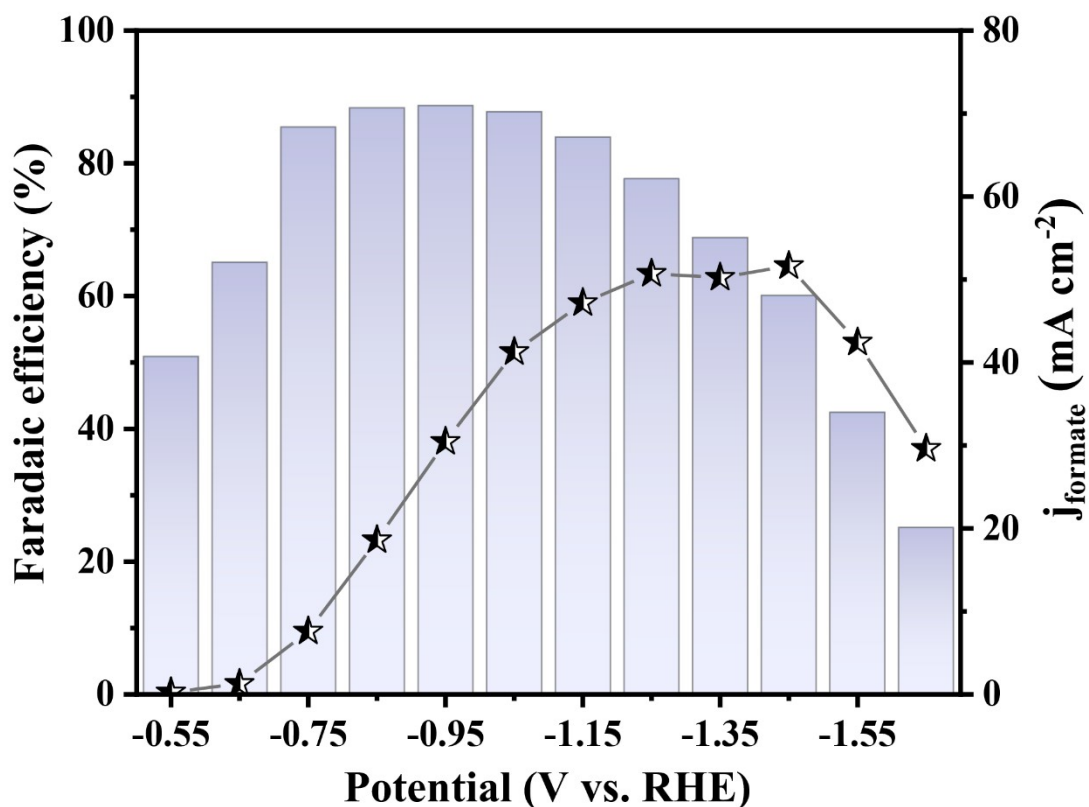


Figure S3. FE_{HCOO-} (histogram) and j_{HCOO-} (star plot) of BOC catalyst at various potentials.

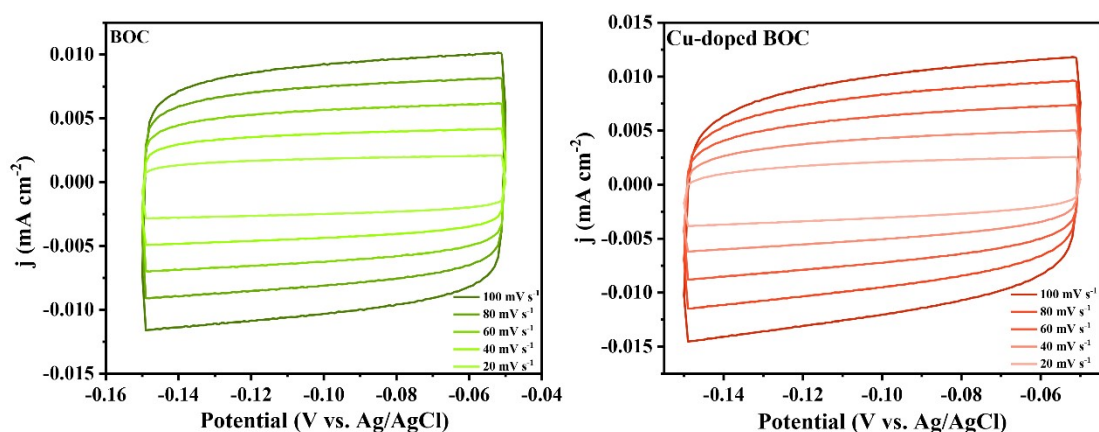


Figure S4. The cyclic voltammetry (CV) curves of (a) BOC, (b) Cu-doped BOC measured in CO₂-saturated 0.5 M KHCO₃ aqueous solution with various scan rates from 20 mV s⁻¹ to 100 mV s⁻¹.

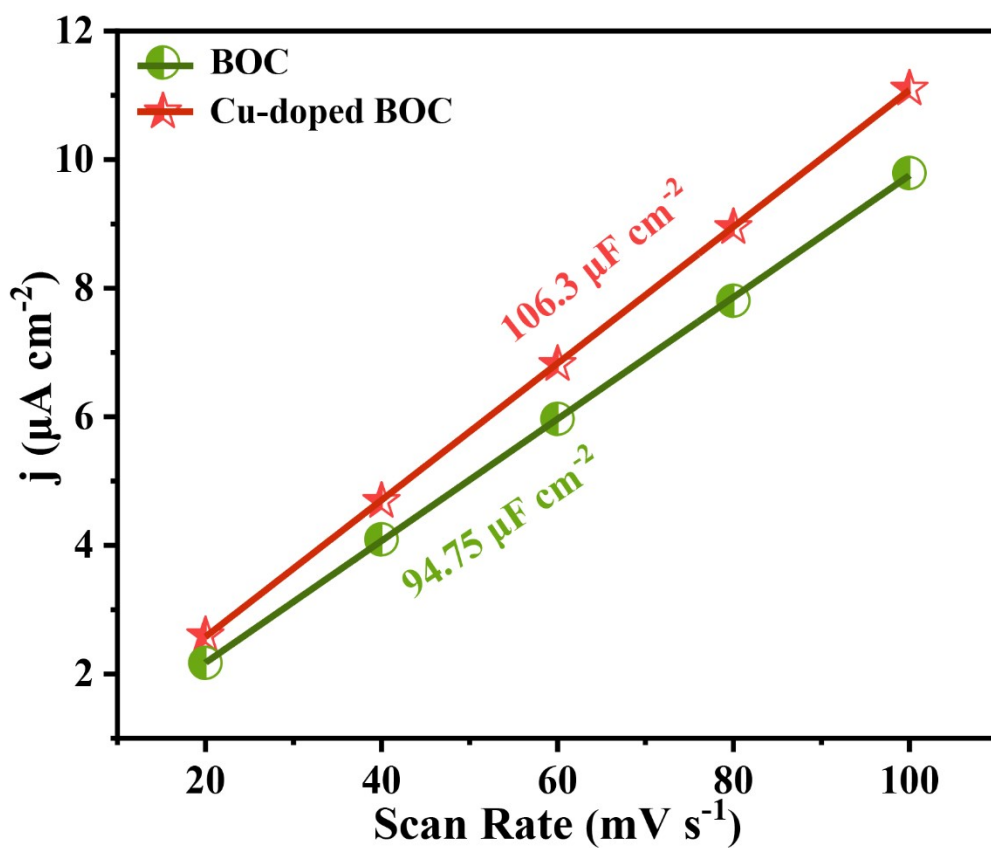


Figure S5. Linear fitting of double-layer capacitive currents vs. scan rates of BOC and Cu-doped BOC catalysts.

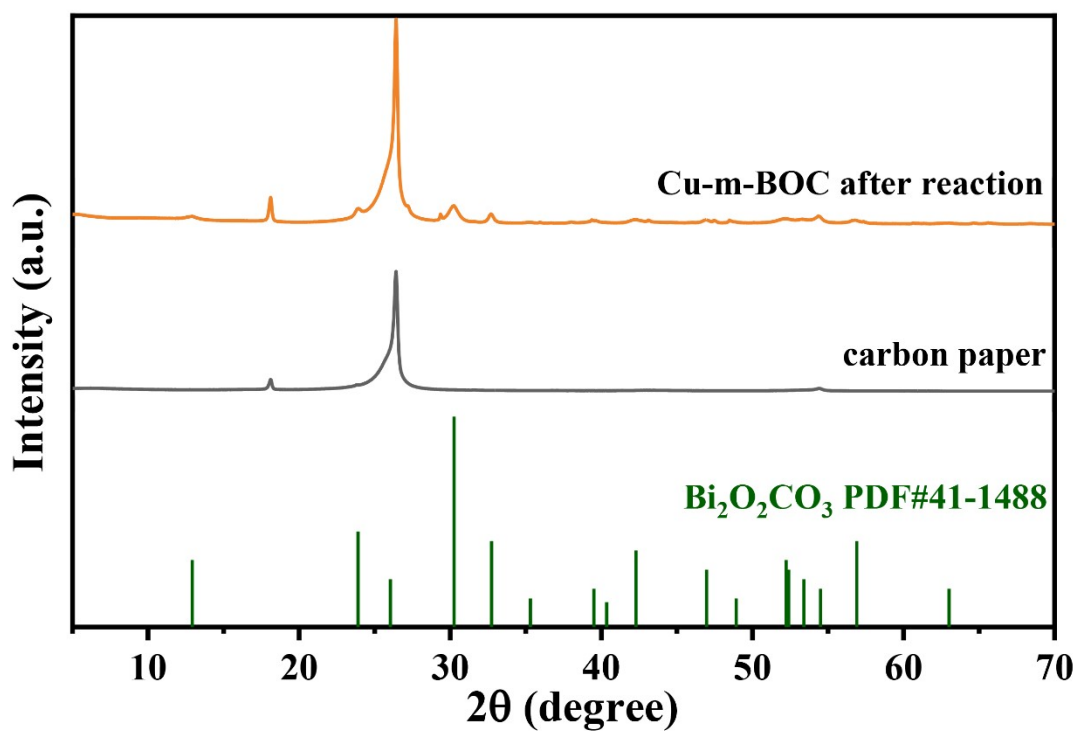


Figure S6. XRD pattern of Cu-doped BOC catalyst after reaction.

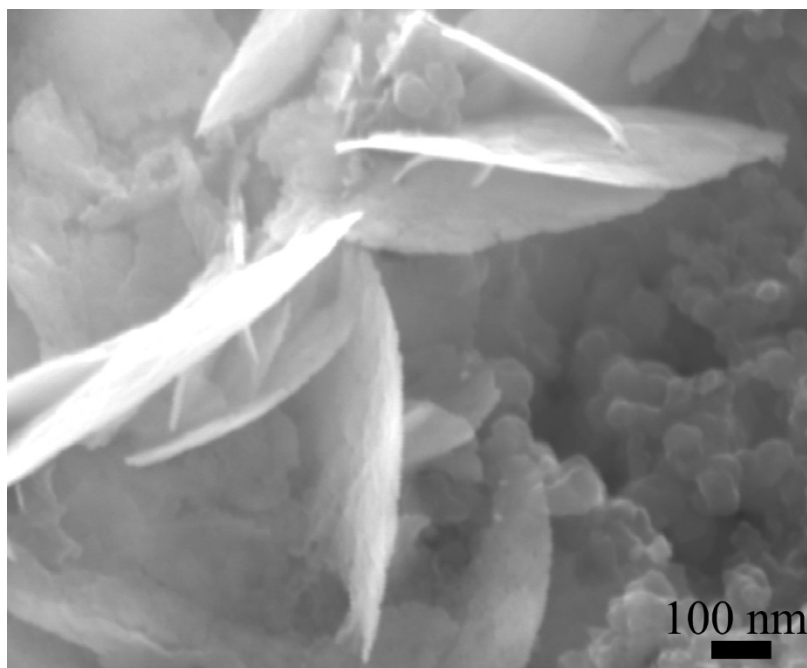


Figure S7. SEM image of Cu-doped BOC catalyst after stability test.

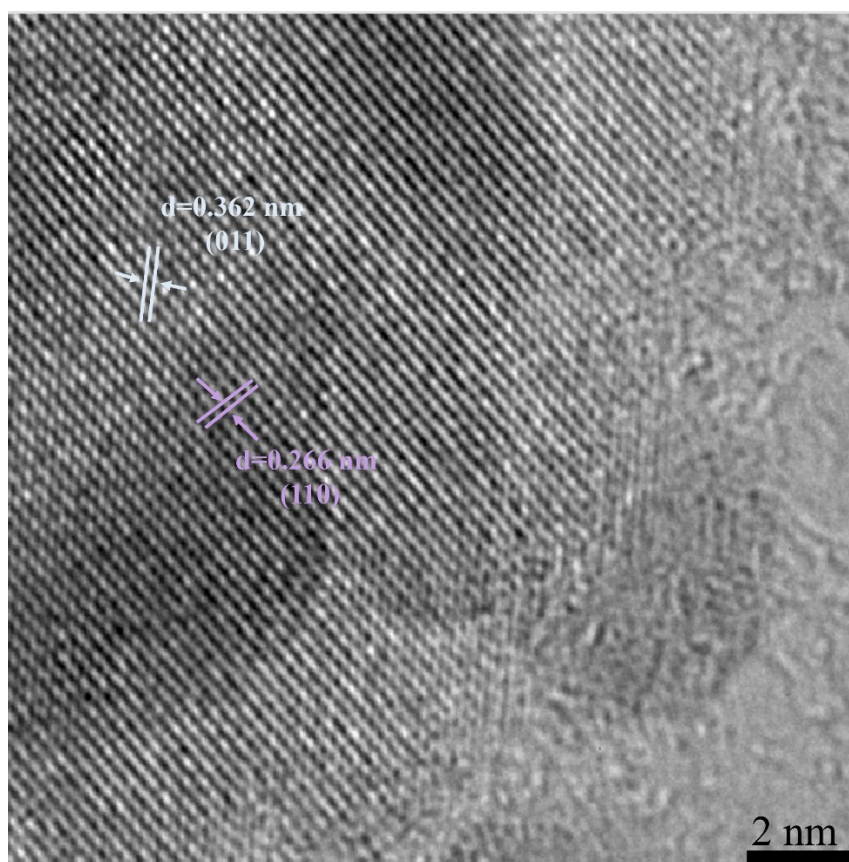


Figure S8. HRTEM image of Cu-doped BOC catalyst after stability test.