Electronic Supplementary Information (ESI)

Designing atomic Ni/Cu pairs on reactive BiOCl surface for efficient photo-chemical HCO_3^--to-CO conversion

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Materials:

Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$), ethylene glycol ($HOCH_2—CH_2OH$), copper chloride ($CuCl_2 \cdot 2H_2O$), nickel chloride ($NiCl_2 \cdot 6H_2O$), polyvinylpyrrolidone (PVP, K30), sodium chloride (NaCl). All these chemicals were of analytical grade and used without further purification. Doubly distilled water was used in all experiments.

Preparation of BOC (BiOCl), Ni_1-BOC, Cu_1-BOC and Ni_1/Cu_1-BOC catalysts:

BOC: 1 mmol $Bi(NO_3)_3 \cdot 5H_2O$, 0.1g PVP were added into 25 mL of ethylene glycol under continuous stirring to form a transparent solution.[1] The transparent solution obtained was then continuously stirred at 70 °C for 5 h, and then solvothermal treated at 150 °C for 24 h. Finally, the powder obtained was washed with H_2O for five times to remove surface residual ions.

Ni_1-BOC, Cu_1-BOC and Ni_1/Cu_1-BOC: 1 mmol $Bi(NO_3)_3 \cdot 5H_2O$, 0.1g PVP were added into 25 mL of ethylene glycol and 6 ml glacial acetic acid mixed solution under continuous stirring to form a transparent solution. Then, 2 mol% $NiCl_2 \cdot 6H_2O$ (here mol% is the molar fraction of $NiCl_2 \cdot 6H_2O$ relative to $Bi(NO_3)_3 \cdot 5H_2O$) and 8 mol% $CuCl_2 \cdot 2H_2O$ were added into the former solutions. For synthesizing Ni_1-BOC or Cu_1-BOC, 10% mol $NiCl_2 \cdot 6H_2O$ or 10 mol% $CuCl_2 \cdot 2H_2O$ was added into the former solutions. The transparent solution obtained was then continuously stirred for 1 h, and then solvothermal treated at 150 °C for 3 h. Finally, the powder obtained was washed with H_2O for five times to remove surface residual ions.

Characterization:

Powder X-ray diffraction (XRD) patterns for the various catalysts and photocatalysts were collected on a Germany Bruker D2 PHASER X-ray diffractometer equipped with a Cu Kα radiation source (λ = 0.15418 nm). X-ray photoelectron spectroscopy (XPS) data were collected on an ESCALAB 250 X-ray photoelectron spectrometer, using non-monochromatic Mg-Kα X-ray as the excitation source, and all binding energy of samples were corrected by referencing the C 1s peak to 284.8 eV of adventitious hydrocarbons. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were collected on a FEI Talos F200X microscope operating at an accelerating voltage of 200 kV. Samples were dispersed on hydrophilic carbon films for the analyses. The instrument was also equipped with EDX elemental mapping. UV-vis diffuse reflectance spectra were collected on Varian

Cary 100 Scan UV-Vis system with $BaSO_4$ as the reflectance standard. Ni, Cu K-edge X-ray absorption fine structure (XAFS) measurements were performed on the 111 beamline of Shanghai Synchrotron Radiation Facility (SSRF). All the measurements were performed at room temperature and atmospheric pressure with a solid sample. The elemental composition of the catalysts was measured using an inductively coupled plasma-optical emission spectrometer (ICP-OES, Varian 710). In situ FTIR spectra was acquired at the Infrared Spectroscopy and Microscopic Imaging End station at the BL01B beamline of the National Synchrotron Radiation Laboratory (NSRL, Hefei, Anhui province). And the spectrum was recorded on a FT-IR spectrometer (German Bruker IFS66v/S).

Photocatalytic HCO_3^-R tests:

Typically, HCO_3^-R experiment was carried out in a glass reactor with a volume of 35 ml. 1 $mol \cdot L^{-1}$ Sodium bicarbonate solution, 10 mL H_2O, 10 mg catalyst were mixed uniformly in an ultrasonic bath. Then, the suspension was purged with Ar (99.999%) for 20 min with 300 W Xe lamp as the light source. During light irradiation, 0.5 mL of gaseous mixture was collected from the reactor at regular time intervals. The products were analyzed by China Education Au-light GC-7920 chromatography, which was equipped with both flame ionization detector (FID) and thermal conductivity detector (TCD).

Electrochemical tests:

Electrochemical measurements were performed on a DH 7000C electrochemical workstation equipped with a three-electrode cell. For electrochemical impedance spectroscopy (EIS) measurements, the working electrode was a glassy carbon electrode coated with catalyst, the counter electrode was a platinum foil, and the reference electrode was a saturated Ag/AgCl electrode. Na_2SO_4 (1 mol L^{-1}, 50 mL) served as the electrolyte with the EIS data collected over the frequency range 0.01-10^5 Hz.

DFT calculation details：

Spin-polarized DFT calculations were performed using the Viennaab initio simulation package (VASP-6.4.2) The exchange–correlation interactions were treated with the Perdew–Burke–Ernzerhof (PBE) functional in the generalized gradient approximation (GGA). The projection augmented wave (PAW) potential method was used to describe the interaction between atomic nuclei and electrons. The

empirical correction method in the Grimme scheme (DFT + D3) was used to describe the van der Waals (vdW) interactions of reactants or intermediates and catalysts.

A 3 × 3 × 2 BiOCl supercell was used as the initial model. A kinetic energy cutoff of 450 eV was set for the plane-wave basis. van der Waals (vdW) corrections were included by adopting the zero damping DFT-D3 dispersion model developed by Grimme et al. A 15 Å-thick vacuum layer was added to the z-direction to separate slabs from their periodic images. The Monk horst–Pack scheme was adopted to sample the Brillouin region with a (3 × 3× 1), k-point mesh grid for supercell structure optimization. The convergence thresholds of energy and force were set to 10^{-6} eV and 0.03 eV $Å^{-1}$, respectively. The free energy correction of the adsorbed molecules was processed using a vaspkit script. The free energy parameter has been widely used to evaluate the catalytic performance of electrocatalysts and it was obtained by calculating the hydrogen electrode model (CHE).

Equation for the change in Gibbs free energy of HCO_3^-RR:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \int CpdT + \Delta GpH$$

Where △E represents the change of total energy between the reactants and the products derived by the DFT technique, ∫CpdT is the enthalpy correction, △ZPE is the zero-point energy correction via frequency analysis, and △S is the change of entropy during each elementary step at a finite temperature of 298.15 K, and $\triangle GpH = k_B T \ln 10 \times pH$ (k_B is the Boltzmann's constant) is caused by the correction of H^+ free energy under different pH values yet not considered in this work.

Table S1. Ni and Cu contents in the as-synthesized samples

Entry	Sample	Ni contents (wt.%)	Cu contents (wt.%)
1	Ni_1/Cu_1-BOC	0.0122	0.0335
2	Ni_1-BOC	0.0231	-
3	Cu_1-BOC	-	0.0425

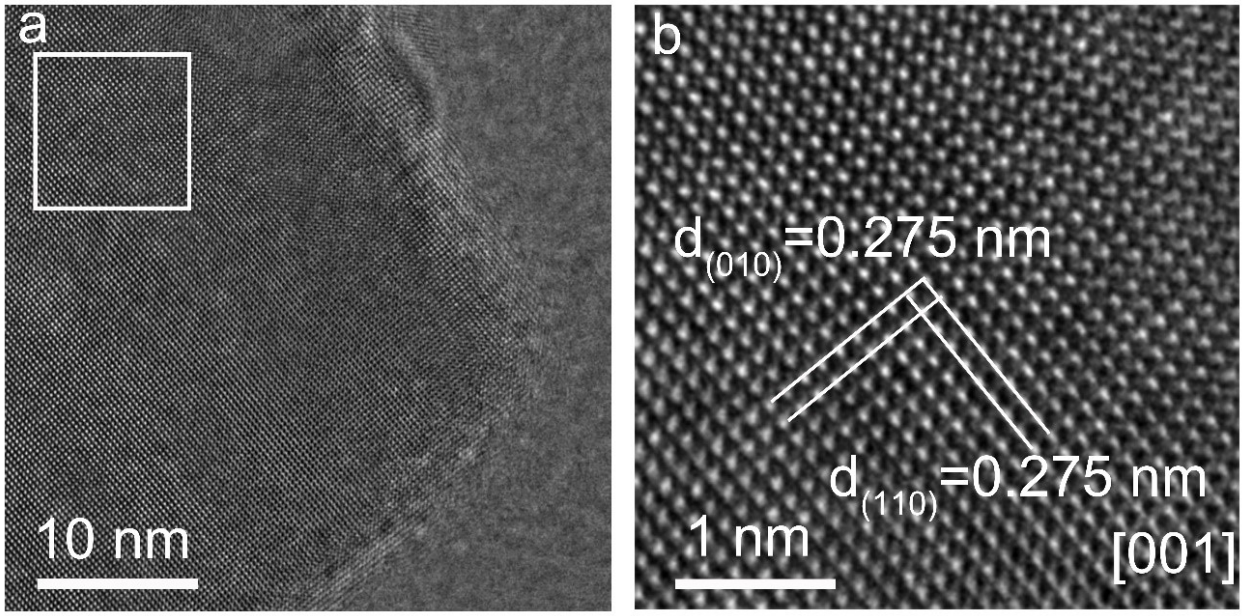

Figure S1. a-c) TEM, HRTEM images of Ni_1/Cu_1-BOC.

Combing with HRTEM images of Ni_1/Cu1-BOC and atomic arrangement of (001) crystal facets in BiOCl (Figure. S1) and the Functions as below:

$hu+kv+lw=0$ Function 1

$u=k_1l_2-k_2l_1$

$v=l_1h_2-l_2h_1$ Function 2

$w=h_1k_2-h_2k_1$

Firstly, both of the lattice spacings were 0.275 nm represented (010) crystal facet and (110) crystal facet. Then, the values of ($h_1k_1l_1$) and ($h_2k_2l_2$) were corresponding to (010) and (110). As a result, the value of [uvw] was [001].

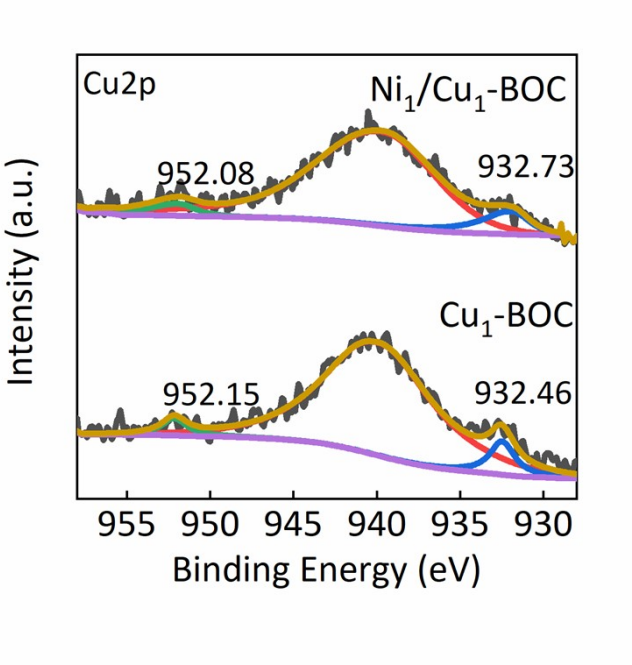

Figure S2. XPS spectra of Cu 2p orbitals collected from Ni_1/Cu_1-BOC and Cu_1-BOC.

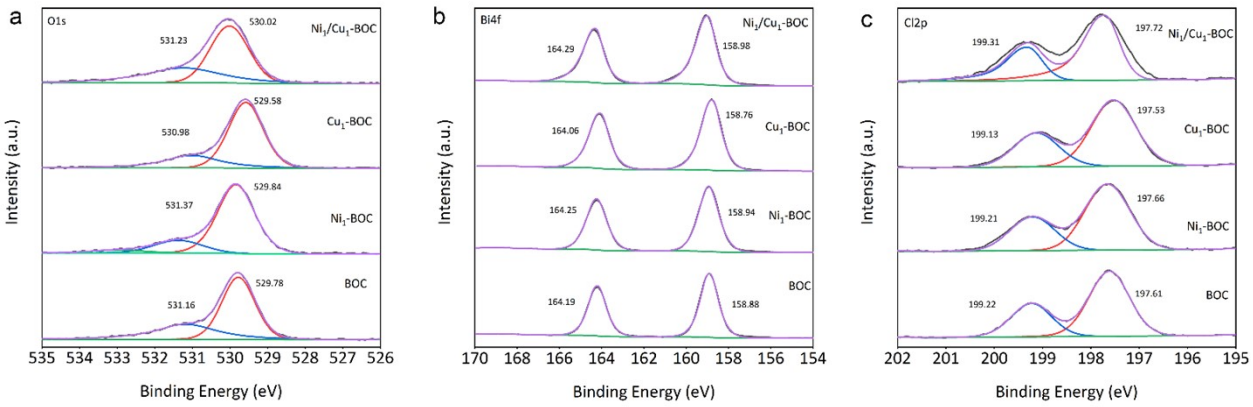

Figure S3. XPS spectra of O 1s, Bi 4f and Cl 2p orbitals collected from Ni_1/Cu_1-BOC, Ni_1 -BOC, Cu_1-BOC and BOC.

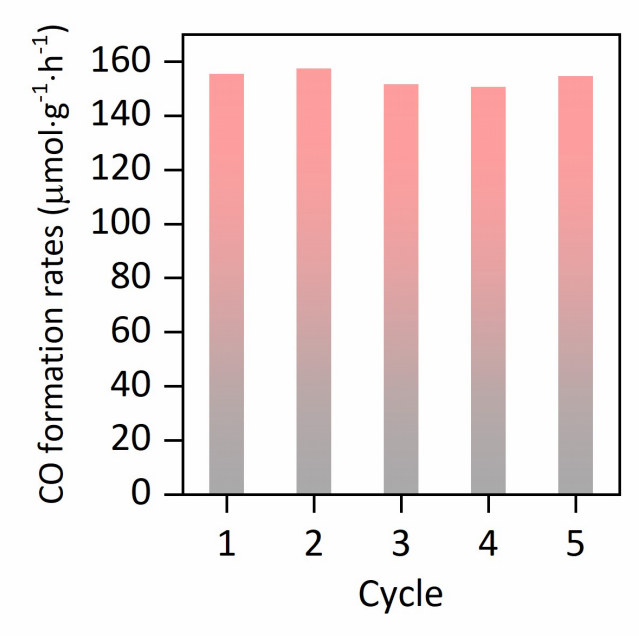

Figure S4. CO formation rates of Ni_1/Cu_1-BOC sample for five cycles during HCO_3^-R.

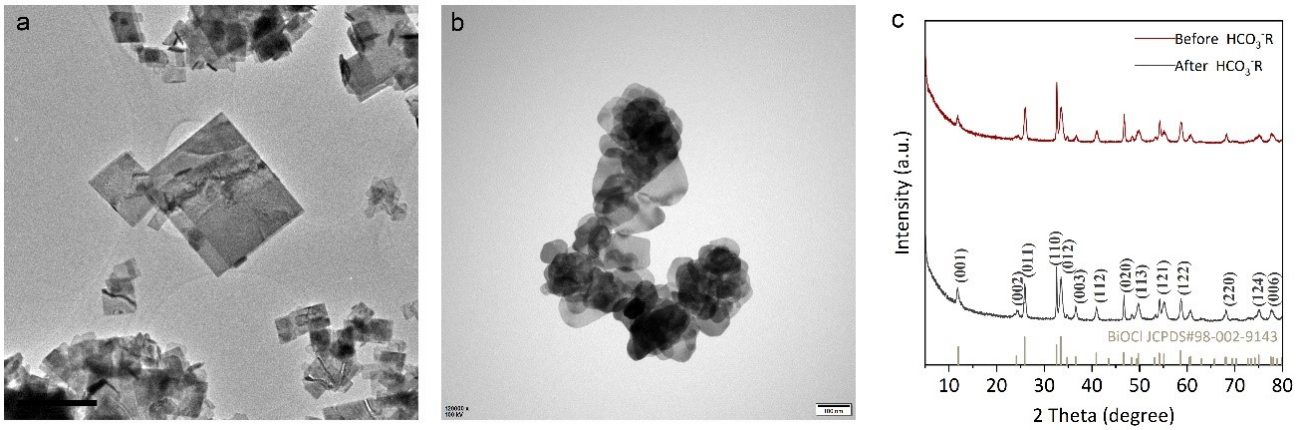

Figure S5. a-c) TEM images and XRD patterns of Ni_1/Cu_1-BOC collected before and after HCO_3^-R reactions.

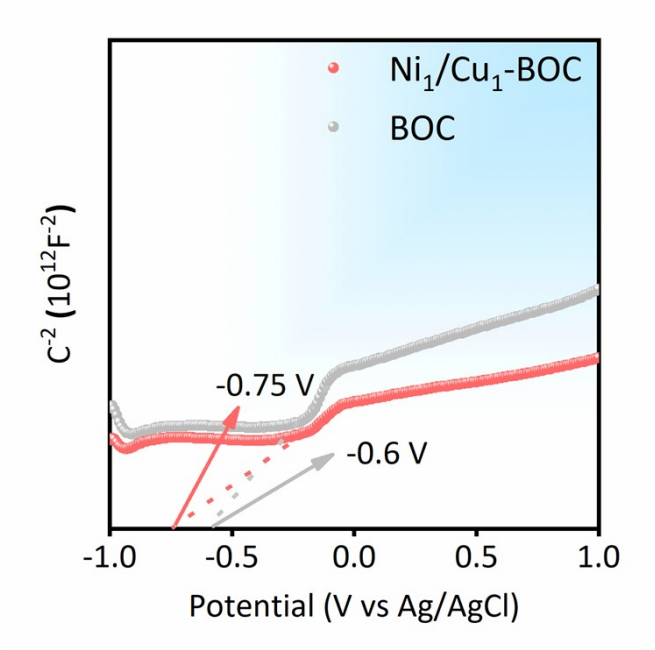

Figure S6. Mott-Schottky plots of Ni_1/Cu_1-BOC and Cu_1-BOC.

The flat band potentials of Ni_1/Cu_1-BOC and BOC were respectively determined to be -0.75 and -0.6 eV. Noted both Ni_1/Cu_1-BOC and BOC were negative semiconductor due to the positive slope in Figure S6, the CB values of these samples were estimated as -0.85 V and -0.7 V (vs. NHE).[2]

According to the reference [2], the calculation functions of energy band structure on all samples were shown as below:

$$E(NHE)=E(Ag/AgCl) + E^0(Ag/AgCl)$$

$$E_{CB}=E(NHE)-0.3V$$

$$E_{VB}=E_g+E_{CB}$$

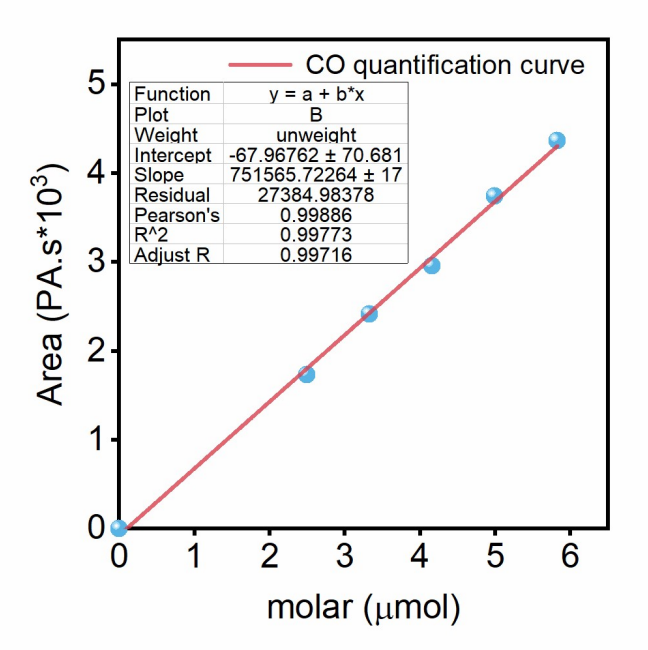

Figure S7. Quantification curves of CO.

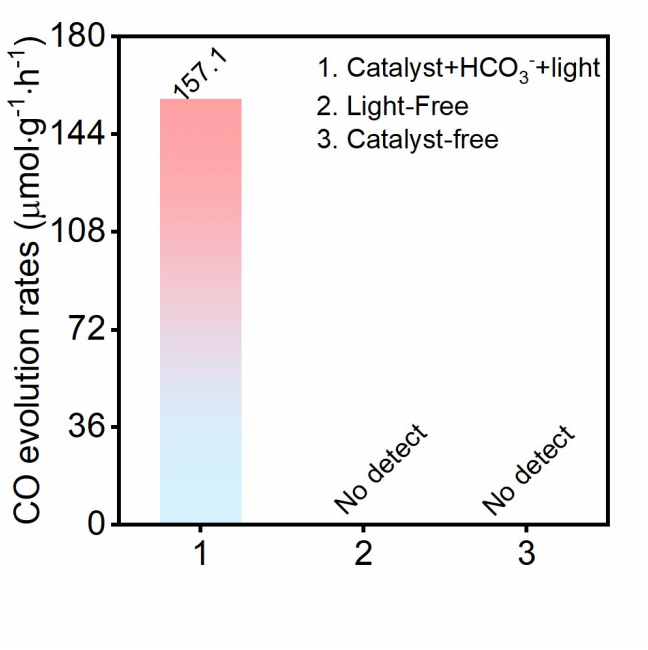

Figure S8. Photocatalytic HCO_3^-R of Ni_1/Cu_1-BOC in light-free and catalyst-free conditions.

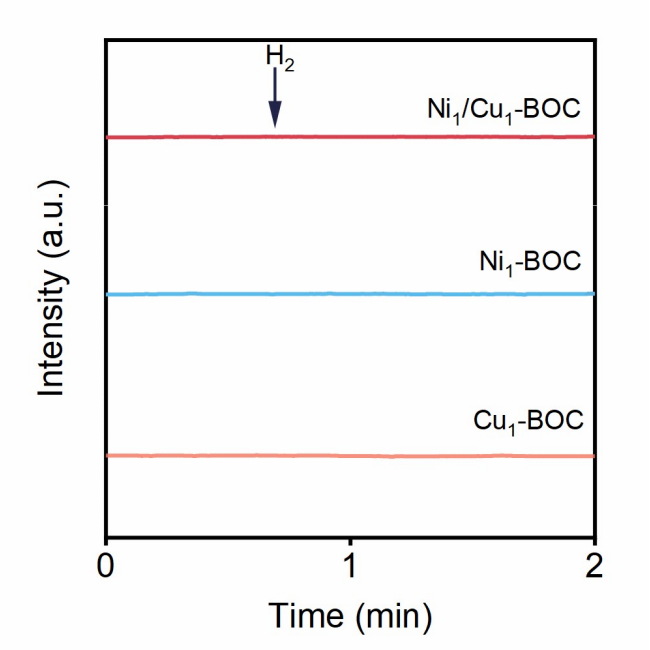

Figure S9. GC signals of H_2 over Ni_1/Cu_1-BOC, Ni_1-BOC and Cu_1-BOC samples after photocatalytic HCO_3^-R reaction.

Reference:

1. J. Jiang, K. Zhao, X. Xiao and L. Zhang, *J. Am. Chem. Soc.*, 2012, **134**, 4473-4476.

2. L. Chen, H. Li, H. Li, H. Li, W. Qi, Q. Zhang, J. Zhu, P. Zhao and S. Yang, *Appl. Catal., B.-Environ.*, 2022, **318**, 121863