Supporting Information

N-doped C Nonocage-Anchored Bismuth Atoms for Efficient CO$_2$ Reduction

Jiayi Li,[a] Lingling Zhang,[b] Shuai Gao,[a] Xingmin Chen,[c] Runjie Wu,[a] Xiao Wang,[b,]* and Qiang Wang[a,]*

[a] Department of Chemistry and College of Elementary Education, Capital Normal University, Beijing 100048, China

[b] State Key Laboratory of Rare Earth Resource Utilization Changchun Institute of Applied Chemistry Chinese Academy of Science Changchun 130022, China

[c] College of Environmental Sciences and Engineering, Nankai University, Tianjin 300350, China.

*E-mail: wangxiao@ciac.ac.cn, qwchem@gmail.com.

Experimental Section

Chemicals.

All chemicals were purchased from Aladdin Chemical Co., Ltd and used without further purification.

Preparation of BiOCl nanoplates.

Typically, 0.972 g of $Bi(NO_3)_3 \cdot 5H_2O$ and 0.800 g of polyvinyl pyrrolidone (PVP) were dissolved in 50 mL of mannitol solution (0.1 M). After stirring for 10 min, 5 mL of saturated NaCl solution dripped into the above mixture, and forming a white suspension. After another 10 min of agitation, the mixture was transferred into a Teflon-lined stainless steel autoclave. The autoclave was maintained at 160 °C for 3 h and subsequently allowed to cool to room temperature. The resulting solid powder was collected by centrifugation and washed with deionized water several times. The final products were dried in oven at 60 °C for 12 h.

Preparation of BiOCl@polydopamine (PDA) precursors.

The above BiOCl (200 mg) were redispersed in 200 mL of distilled water 240 mg of Tris(hydroxymethyl)aminomethane. After that, 100 mL of distilled water containing 200 mg of dopamine was added with continuous stirring for 5 h. The product were collected by filtration, washed several times with ethanol and dried at 60 °C.

Preparation of Bi-NC$_{box}$-900 and Bi-NC$_{box}$-900.

The BiOCl@PDA (200mg) was annealed in argon atmosphere at 900 °C and 800 °C for 5 h to prepare Bi-NC$_{box}$-900 and Bi-NC$_{box}$-900, respectively.

Characterization.

Field emission scanning electron microscope (FEI, Qunta250, USA) and transmission electron microscope (FEI, TECNAI G2) accelerating voltage of 20 kV were employed to characterize the morphologies of all samples. Bruker D8 Focus powder X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å) was used to determine the XRD pattern.X-ray photoelectron spectroscopy (XPS) analyses were performed by ESCALAB-MKII 250 photoelectron spectrometer with Kα radiation. CHI 660E electrochemistry workstation (CH Instruments, Inc., Shanghai) was used to carry out electrochemical tests. Bi EXAFS data were measured at BL14W1 beamline in shanghai synchrotron Radiation Facility.

Electrochemical measurements.

5 mg of catalysts powders were suspended in 950 µL of ethanol solution with 5 µL of Nafion (5 wt. %) to form a homogenous ink assisted by ultrasound 1 h. Then, 200 µL of the dispersion was loaded onto a carbon paper electrode with an area of 1 × 1 cm^2 and dried in an oven at 60 °C. The electrochemical measurements were performed with a CHI 660E electrochemical workstation in an H-type cell, which consists of two compartments separated by Nafion 117 membrane at room temperature. In this gas-tight three-electrode setup, platinum plate and Ag/AgCl electrode (3.5 M KCl) were used as counter electrode and reference electrode, respectively. CO_2-saturated 0.5 M $KHCO_3$ (pH ≈ 7.22) was used as electrolyte. The volume of electrolyte is 40 mL for both anode and cathode in H-type cell. All potentials measured were calibrated to the reversible hydrogen electrode (RHE) reference scale using

$$E_{RHE} = E_{Ag/AgCl} + 0.0591 \times pH + 0.2046$$

The linear sweep voltammetry (LSV) was tested at a sweep rate of 10 mV s^{-1}. Potentiostatic measurement was conducted over the potential range from -0.4 to -0.8 V *vs.* RHE. The current density was calculated by normalizing the current to the corresponding geometric surface area. The cyclic voltammetry (CV) curves under different scan rate were used to estimate double layer capacitances (C_{dl}). The CV was carried out at 10, 15, 20, 25, 30 mV s^{-1} in a potential window of 0.1 V~ 0.2 V *vs.* RHE. The CO partial current density (J_{CO}) shown in Figure 2c was calculated from the formula provided in the literature (*Chinese J. Catal.* 2023, 48, 117–126). The formula is as follows:

$$FE_{CO} = C_{co} \times S \times (\frac{2FP}{RT}) \div I_{total}$$

$$J_{CO} = C_{CO} \times S \times (\frac{2FP}{RT}) \div A$$

where C_{CO} refers to the concentrations of CO measured by GC, S (flow rate of CO_2), F (Faraday constant) = 96485 C mol^{-1}, P (atmospheric pressure) = 101300 Pa, R (gas constant) = 8.314 J mol^{-1} K^{-1}, T (thermodynamic temperature) = 298.15 K, A refers to the geometric area of the electrode, I_{total} is the measured current.

In this electrochemical test, the electrode area is 1 cm^2, that is, A = 1, so J_{CO} is also calculated by the following formula:

$$J_{CO} = FE_{CO} \times I_{total}$$

***Products Analysis*:**

For CO_2 reduction experiments, the electrolyte was purged with CO_2 for 30 min before the measurement. The electrolyte in the cathodic compartment was stirred at a rate of 400 rpm during electrolysis. The flow rate of CO_2 was controlled by electronic

flowmeter. The gas products of CO_2 reduction were detected by on-line Gas chromatograph (GC, PANNA 91Plus), which equipped with a thermal conductivity detector (TCD), a methanator assisted flame ionization detector (FID) were used to detect the products in the process. The liquid products were detected by Bruker NMR spectrometers (AVANCE-III HD 500). The reduced product of H_2 was detected by TCD. CO was detected by FID. N_2 (99.999%) was used as carrier gas.

Calculation of Faradic efficiency (FE):

For gas product:

$$FE = (nvpVF/IRT) \times 100\%$$

where n is the number of electrons transferred (For H_2 and CO, n =2), v (vol %) is the volume concentration of CO and H_2 in the outlet gas from the H-type cell, p = 1.013 × 10^5 Pa, V is the gas flow rate (20 mL min^{-1}, calibrated by mass flow controller) at the exit of the cell, F is Faradaic constant (96485 C mol^{-1}), I is the steady-state total current density (A), R is the ideal gas constant (8.3145 J mol^{-1} K^{-1}), T = 298.15 K.
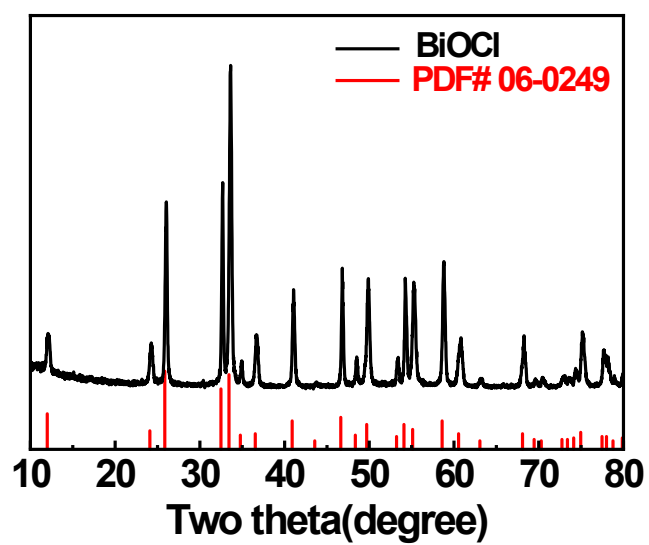
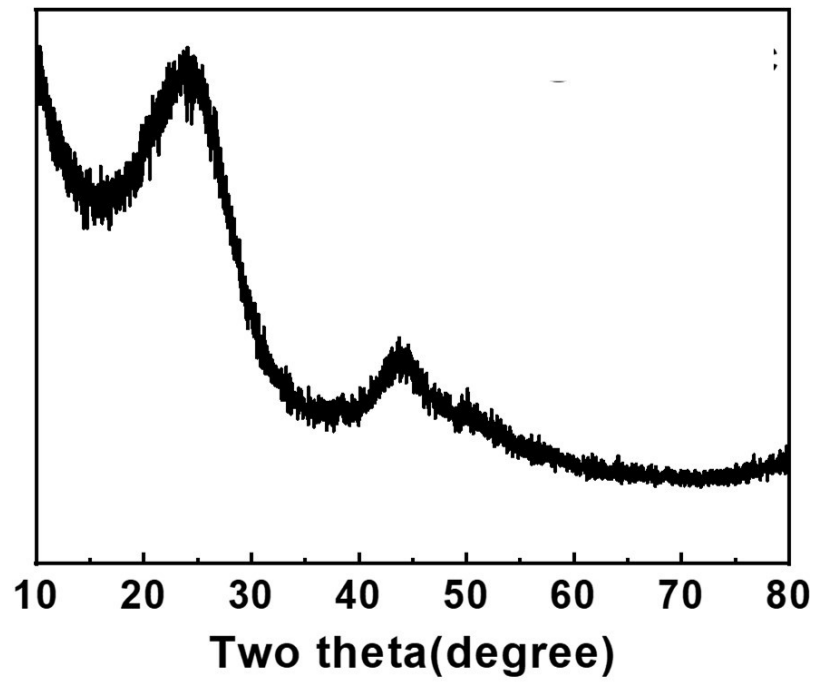**Figure S1.** XRD pattern of the BiOCl nanoplates.
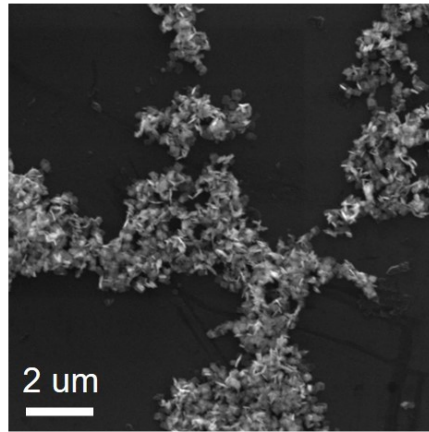
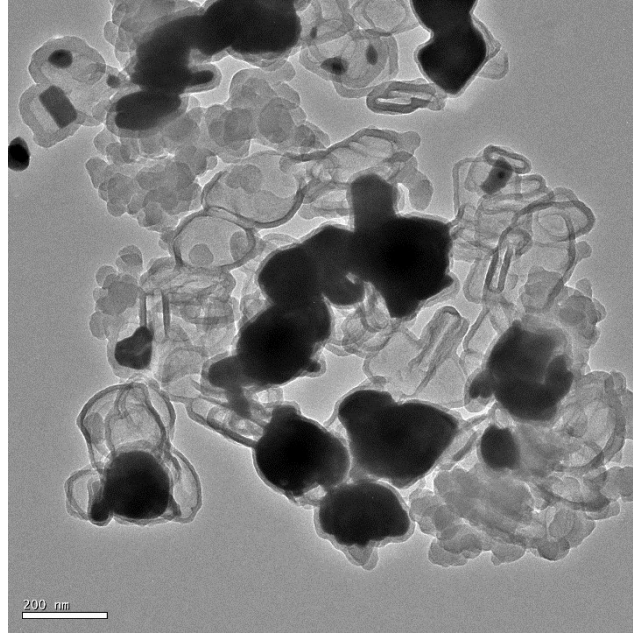**Figure S2.** SEM image of the BiOCl nanoplates.
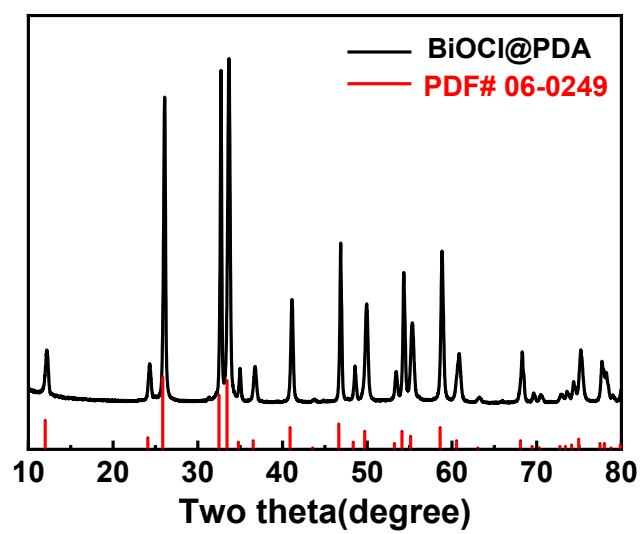
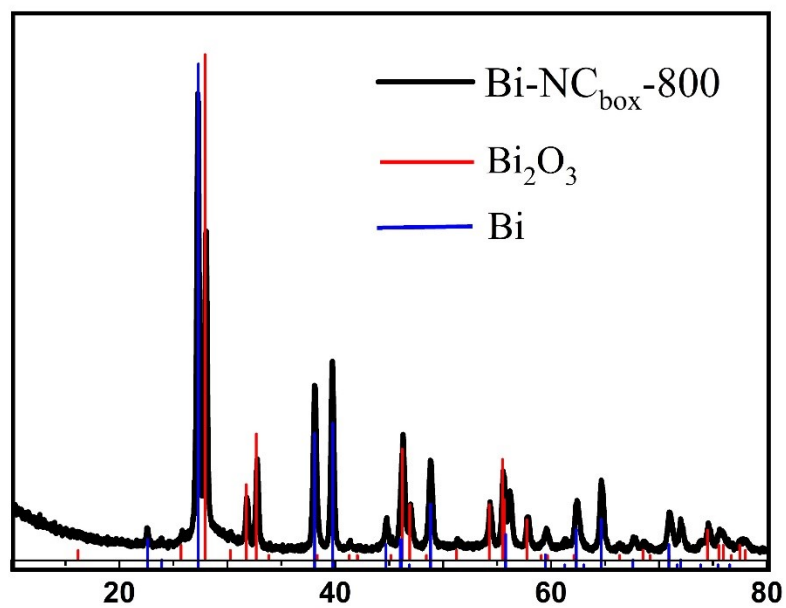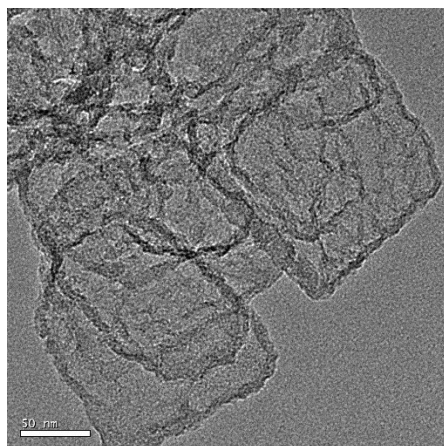**Figure S3.** XRD pattern of the BiOCl@PDA precursors.

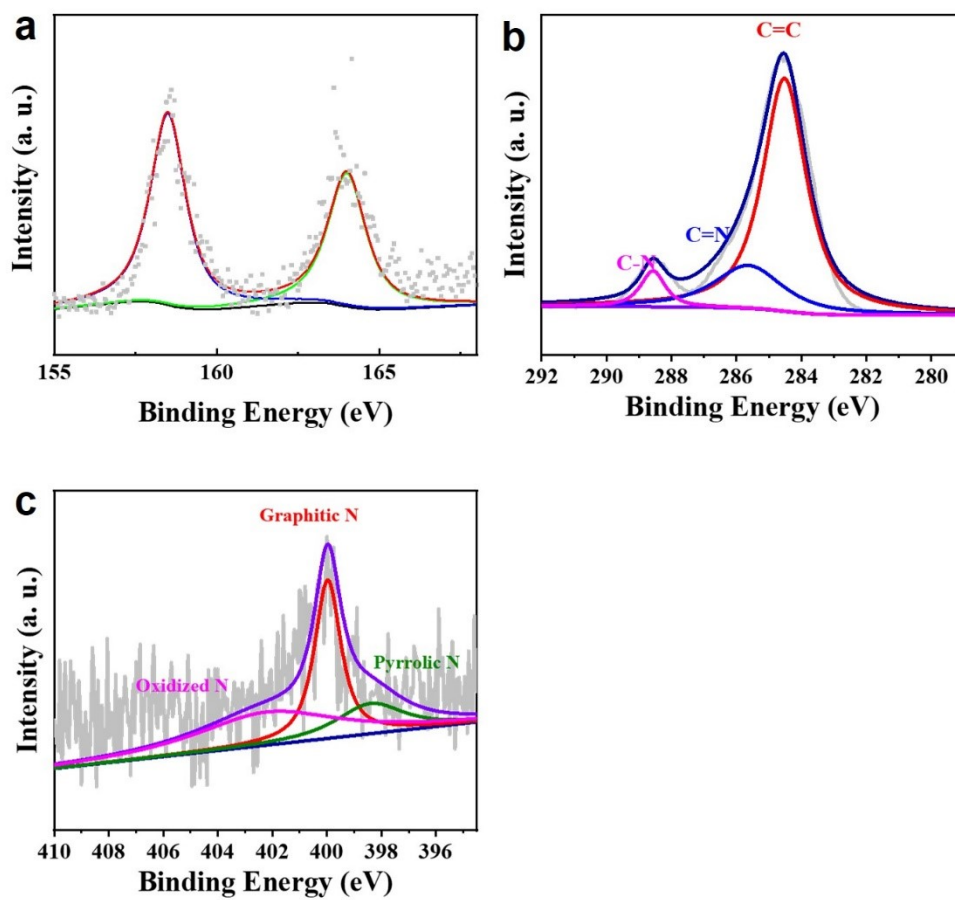**Figure S4.** XRD pattern of the Bi-NC$_{box}$-900 catalyst.

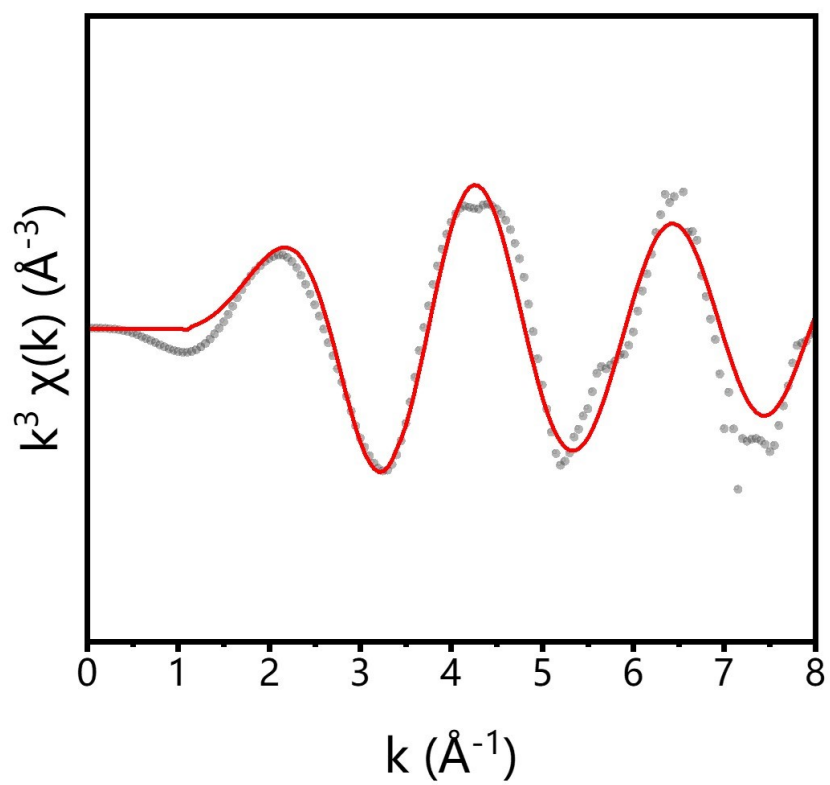**Figure S5.** TEM image of the Bi-NC$_{box}$-800 catalyst.

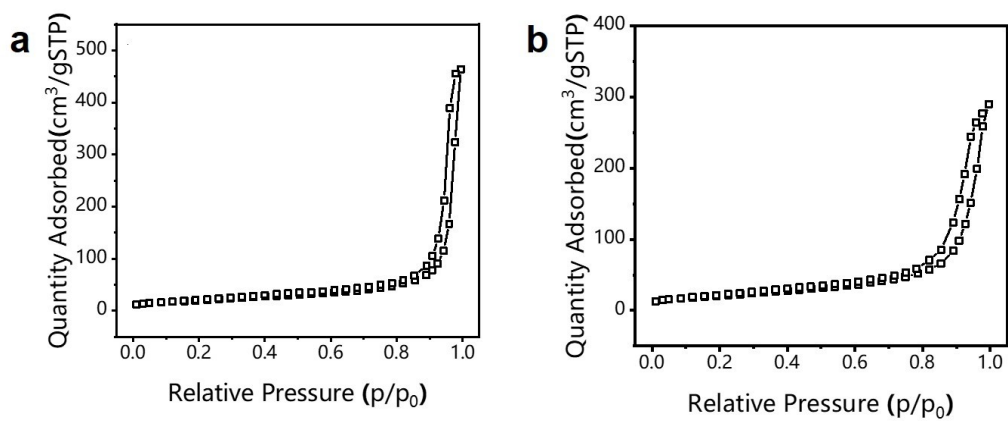**Figure S6.** XRD pattern of the Bi-NC$_{box}$-800 catalyst.

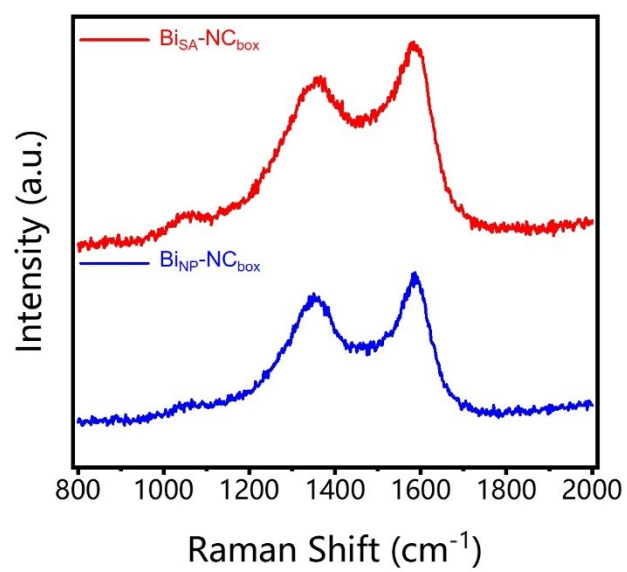**Figure S7.** TEM image of the Bi-NC$_{box}$-1000 catalyst.

Figure S8. XPS spectra of Bi 3d, C 1s and N 1s in the Bi-NC$_{box}$-900 catalyst.
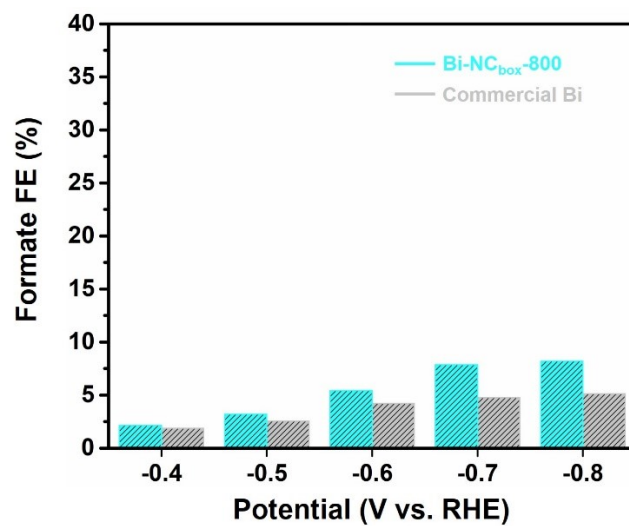
Figure S9. EXAFS k space fitting curves of Bi-NC$_{box}$-900.

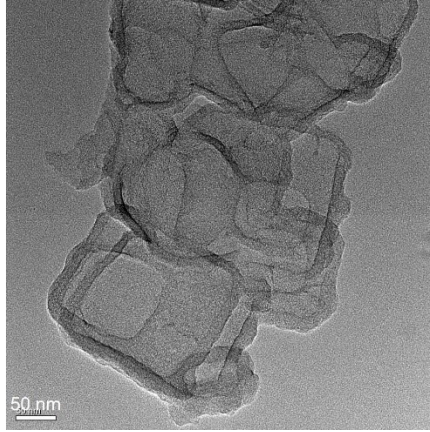**Figure S10.** BET surface area measurement of the (a) Bi-NC$_{box}$-900 and (b) Bi-NC$_{box}$-800 catalysts.

Figure S11. Raman spectra of the Bi-NC$_{box}$-900 and Bi-NC$_{box}$-800 catalysts.

Figure S12. Formate FE values obtained over Bi-NC$_{box}$-800 and commercial Bi at different potentials.

Figure S13. TEM image of the Bi-NC$_{box}$-900 catalysts after stability test.

Table S1. The contents of Bi in Bi-NC$_{box}$-900 and Bi-NC$_{box}$-800.

Sample	Bi-NC$_{box}$-900	Bi-NC$_{box}$-800
Bi content	0.35%	6.2%

Both Bi-NC$_{box}$-900 and Bi-NC$_{box}$-800 are obtained from BiOCl@PDA precursors. When calcining at 800 ^{o}C, a certain amount of Bi element is remained in the product to form bigger Bi NPs (Bi-NC$_{box}$-800). At higher temperature, such as 900 ^{o}C, almost all Bi element is evaporated, leaving Bi SAs in the final product (Bi-NC$_{box}$-800). Therefore, the Bi content of Bi-NC$_{box}$-800 is much higher than of Bi-NC$_{box}$-900.

Table S2. The contents of N in Bi-NC$_{box}$-900 and Bi-NC$_{box}$-800.

Sample	Bi-NC$_{box}$-900	Bi-NC$_{box}$-800
N content	2.64 %	3.31 %

Table S3. Currently Reported Bi-based Catalysts for CO_2RR.

Catalyst	Electrolyte	FE (max)	Applied potential (vs. RHE)	j at FE (max)	Reference
Bi-NC$_{box}$-900	0.5 M KHCO$_3$	FE$_{CO}$ = 91.7 %	-0.6 V	13.8 mA cm^{-2}	This work
Bi-PVP/CC600	0.5 M KHCO$_3$	FE$_{HCOOH}$ = 86 %	-0.83 V	24.5 mA cm^{-2}	Appl. Catal. B Environ. 2021, 284, 119723
CuBi-#8	0.1 M KHCO$_3$	FE$_{HCOOH}$ = 96 %	-0.99 V	12.5 mA cm^{-2}	Colloid Surf. A-Physicochem. Eng. Asp. 2021, 631, 127637
BiPdC	0.5 M KHCO$_3$	FE$_{HCOOH}$ = 63.4 %	-0.97 V	6.2 mA cm^{-2}	ACS Appl. Nano Mater. 2022, 5, 12387−12394
Bi-ZnO	0.5 M KHCO$_3$	FE$_{C1}$ = 75.1 %	-1.0 V	17.13 mA cm^{-2}	ChemCatChem 2022, 14, e202201076
Bi/Bi$_2$O$_3$–O$_v$	0.5 M KHCO$_3$	FE$_{HCOOH}$ = 90 %	-0.8 V	2.5 mA cm^{-2}	Energy Technol. 2022, 10, 2200561
Bi$_{45}$Sb$_{55}$ catalyst	0.5 M KHCO$_3$	FE$_{HCOOH}$ = 76.7 %	-1.0 V	58 mA cm^{-2}	J. Electrochem. Soc. 2023, 170, 056509