

Supporting Information

Coordinating the Edge Defects of Bismuth with Sulfur for Enhanced CO₂ Electroreduction to Formate

*L. Lv, R. Lu, J. Zhu, R. Yu, W. Zhang, E. Cui, X. Chen, Y. Dai, L. Cui, J. Li, L. Zhou, W. Chen, Z. Wang, L. Mai**

Supplementary Methods.

Chemicals. Bismuth Bromide (BiBr_3), thiourea ($\text{CH}_4\text{N}_2\text{S}$), Ethylenediaminetetraacetic acid (EDTA), Potassium bicarbonate (KHCO_3), Potassium hydroxide (KOH) were purchased from Aladdin Industrial Inc. (Shanghai, China). Nafion solution (5 wt.%) was purchased from Alfa Aesar Chemical Co. Analytical grade ethanol was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the chemicals were used without further purification.

Materials synthesis. BiBr_3 (5 mmol), thiourea (4.6 mmol), EDTA (0.2 g), and ethanol (60 mL) were first mixed under vigorous stirring for 1 h at room temperature. The primrose yellow suspension gradually turned into a bright yellow transparent solution. Then, the mixed solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave. The sealed autoclave was heated at 180 °C for 72 h in an oven, and then naturally cooled to ambient temperature. The resulting precipitates were washed with deionized water and ethanol to remove residual ions and dried at 80 °C for 4 h.

Characterization. The phase analysis of catalysts was performed on D8 Advance X-ray diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). JEOL-7100F scanning electron microscope (SEM) and double spherical aberration corrected transmission electron microscope (Titan Cubed Themis G2 300/Titan Cubed Themis G2 30) was used to characterize the morphology and elemental distribution of the catalysts. XPS measurements were performed on AXIS SUPRA, Kratos. The powder XAFS spectrum of Bi L_3 -edge was collected at room temperature in the transmission mode at Beamline 12-BM-B at the Advanced Photon Source (APS). Mass spectra were collected by GC-MS (Agilent 7890b/5977b).

Electrochemical measurements. All electrochemical tests were performed using an electrochemical workstation (Autolab PGSTAT 204, Metrohm) with a maximum current output of ± 400 mA. The ECO₂RR performance of the as-prepared catalysts was implemented in a flow cell system. For the flow cell system, an electrocatalyst ink was prepared using a mixture of 1.9 mL ethanol, 0.1 mL Nafion solution, and 20 mg catalyst, and the ink was sprayed onto the GDE to yield a catalyst loading of 1 mg cm⁻². An Ag/AgCl electrode was used as the reference electrode and nickel foam was used as the counter electrode. The working and reference electrodes were separated by an anionic exchange membrane (AEM, Sustainion® X37-50 grade 60, dioxide material). 1.0 M KOH was used as the electrolyte and the flow rate of CO₂ was set at 50 sccm min⁻¹. The polarization curves were recorded at a scan rate of 10 mV s⁻¹. The potential values were referenced to the RHE according to the formula $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.198 + 0.059 \times \text{pH}$. All potentials were recorded without iR-correction.

Product analysis. The gaseous products were detected by online GC (GC2014C, Shimadzu) equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID) detector. Argon (Praxair 99.999%) was used as the carrier gas and the GC was calibrated with H₂, CO, CH₄, and C₂H₄. Each gas phase product analysis time is set at 7 minutes. The FEs for gas products, such as H₂, and CO, were calculated as follows:

$$\text{FE (\%)} = \frac{NF \times \left(\frac{v}{60}\right) \times \left(\frac{y}{24.5 \times 10^9}\right)}{i} \times 100\% \quad (1)$$

where N is the number of electrons required for products (for H₂, CO, and HCOO⁻, N is equal to 2), y (ppm) is the volume concentration of the gas product, v (sccm) is the gas flow rate, i (A) is the collected cell current, F is the Faraday constant (96,500 C mol⁻¹).

Liquid products were quantified by analyzing the collected electrolytes using NMR (Bruker Avance III, 600 M). A known concentration of dimethyl sulfoxide (DMSO) is used as an interior label. Based on the ^1H NMR analysis, the amounts of products were quantified by calculating the relative peak area of HCOO^- (1.09 ppm) and DMSO (2.6 ppm). The FE for HCOO^- was calculated as follows:

$$\text{FE (\%)} = \frac{nNF}{Q} \times 100\% \quad (2)$$

where n is the measured amount of HCOO^- (mol), N is the number of electrons required for each product, and Q is the recorded total charge during the operation.

***In-situ* X-ray absorption measurements.** The Bi L_3 -edge XANES and EXAFS spectra were collected at room temperature in fluorescence excitation mode at Beamline BL11B of the Shanghai Synchrotron Radiation Facility (SSRF) with a ring electron current of 250 mA at 3.5 GeV. The electrochemical measurements were performed by a three-electrode system using an electrochemical workstation (Autolab PGSTAT 204, Metrohm). The electrocatalyst inks were prepared using a mixture of 0.1 mL deionized water, 0.85 mL ethanol, 0.05 mL Nafion solution, and 5 mg of the catalysts followed by ultrasonication for 30 min, and then 0.2 mL of the ink was uniformly loaded onto a CP. A commercial electrolytic cell (Zhongkewanheng) was used to accommodate the electrochemical reaction. CO_2 -filled 0.5 M KHCO_3 was used as an electrolyte. Carbon rod and Ag/AgCl were used as the counter electrode and reference electrode, respectively. The signal collection is achieved by performing the chronoamperometry test at the target potential for 10 min.

***In-situ* Raman measurements.** Raman spectra were obtained by Horiba LabRAM HR Evolution. The Raman spectra were acquired with a He/Ne laser of $\lambda = 532$ nm and 4.9 mW. The multi-potential

chronoamperometry test was performed by an electrochemical workstation (Autolab PGSTAT 204) in a customized Teflon cell with a CO₂-filled 0.1 M KHCO₃ electrolyte. A catalyst-supported gold electrode (GE, diameter = 0.3 cm) worked as the working electrode, an Ag/AgCl electrode as the reference electrode, and a polished platinum wire as the counter electrode. The preparation process of electrocatalysts ink is the same as the process described above. Then, 5 μL of the ink was uniformly loaded onto a freshly polished GE.

***In-situ* ATR-SERIES measurements.** The *in-situ* ATR-SERIES spectra were collected by a FT-IR spectrometer (Nicolet iS50, Thermo Scientific) equipped with MCT-A detector. The catalysts inks were prepared using a mixture of 5 mg electrocatalysts, 0.95 mL ethanol, and 50 μL of Nafion solution. 10 μL of ink was dropped onto the surface central area (confined by an O-ring with $\Phi = 8$ mm) of a hemicylindrical Si prism on which an Au film is chemically deposited. The Si prism was assembled in a spectroelectrochemical cell with Pt wire as a counter electrode, Ag/AgCl electrode as a reference electrode, and 0.1 M KHCO₃ solution as electrolytes. All spectra were collected at a resolution of 4 cm⁻¹ and each single-beam spectrum was an average of 200 scans. An Autolab PGSTAT 204 electrochemical workstation (Metrohm) was used for potential control. High pure CO₂ is continuously introduced into electrolytes during the reaction.

DTF calculations. DFT calculations were constructed and implemented in the Vienna ab initio simulation package (VASP).^[1,2] the electron exchange and correlation energy was treated within the generalized gradient approximation in the Perdew–Burke–Ernzerhof functional (GGA-PBE),^[3] the calculations were done with a plane-wave basis set defined by a kinetic energy cutoff of 450 eV. The

k-point sampling was obtained from the Monkhorst–Pack scheme with a $(3 \times 3 \times 1)$ mesh for optimization and a $(4 \times 4 \times 1)$ mesh for the calculations of electronic structure. The geometry optimization and energy calculation are finished when the electronic self-consistent iteration and force were reach 10^{-5} eV and 0.02 eV \AA^{-1} , respectively.

The free energy is calculated based on $\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$, where ΔE is the energy change obtained from DFT calculations, ΔE_{ZPE} is the difference between the adsorbed state and gas, which was calculated by summing vibrational frequency for all model based on the equation: $E_{ZPE} = 1/2\sum h\nu_i$ (T is the temperature (298.15 K) in the above reaction system), and ΔS represents the difference on the entropies between the adsorbed state and gas phase. Besides, the energy of proton/electron pair is equal to half the energy of hydrogen molecule according to the computational hydrogen electrode (CHE) method.^[4]

References

- [1] Kresse G, Furthmüller J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set [J]. Computational Materials Science, 1996, 6: 15-50
- [2] Kresse G, Furthmüller J. Efficient iterative schemes for ab initio total-energy calculations using a plane wave basis set[J]. Physical Review B, 1996, 54(11): 169-185.
- [3] Grimme S, Antony J, Ehrlich S, et al. Generalized gradient approximation to the angle- and system-averaged exchange hole[J]. J Chem Phys, 2010, 132(15): 154104.
- [4] Nørskov J K, Bligaard T, Logadottir A, et al. Trends in the Exchange Current for Hydrogen Evolution[J]. Journal of The Electrochemical Society, 2005, 152(3): 23-26.

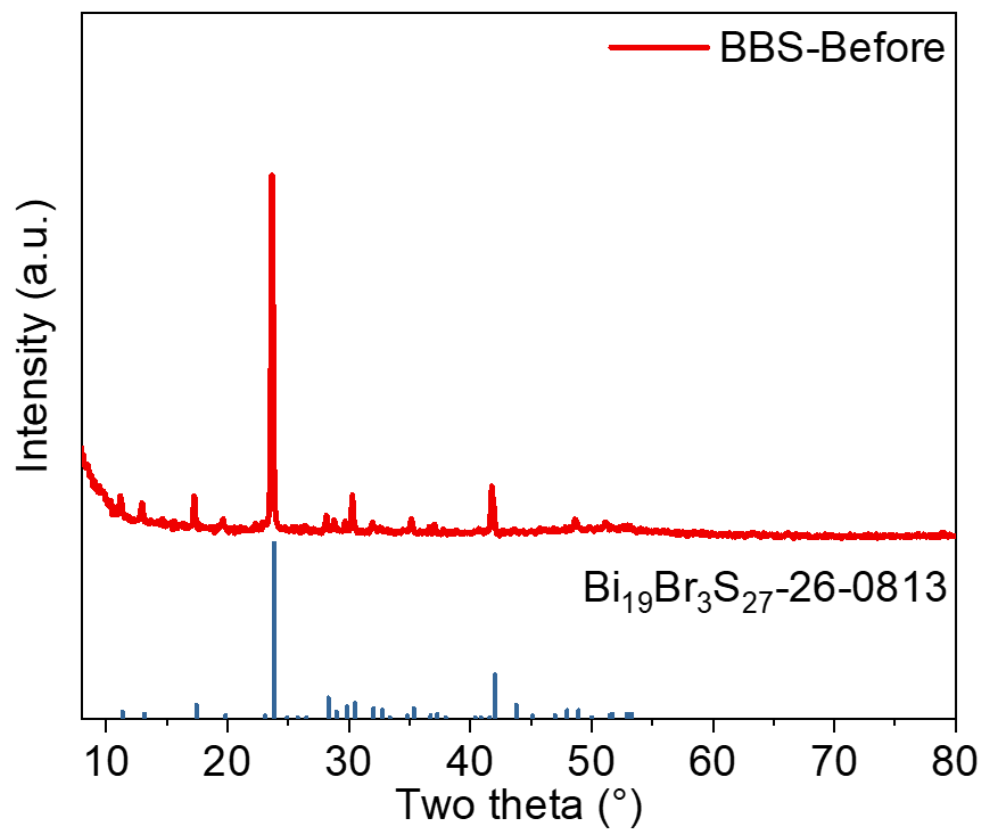


Figure S1 XRD pattern of $\text{Bi}_{19}\text{Br}_3\text{S}_{27}$.

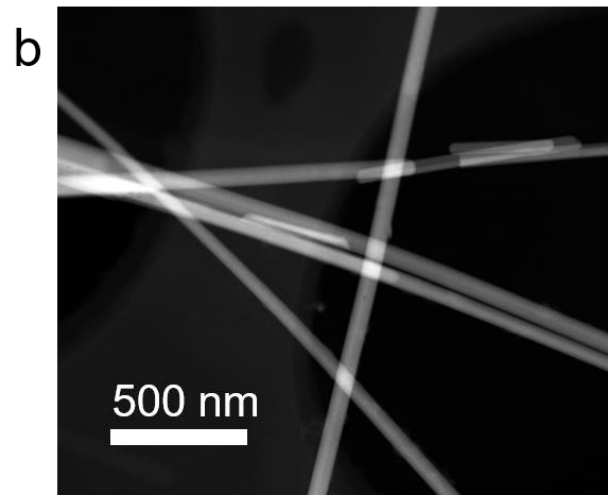
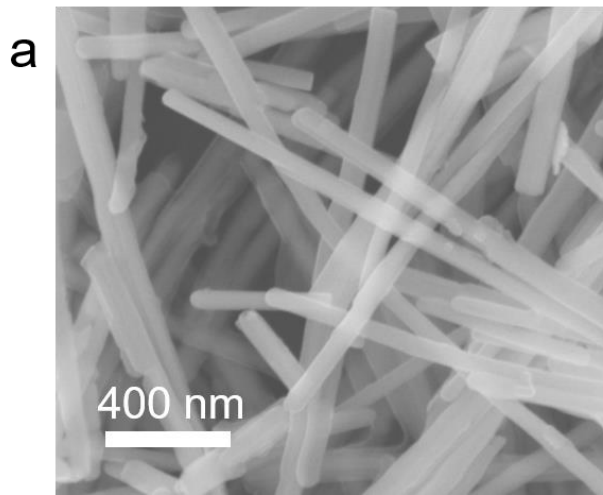


Figure S2 (a) SEM image and (b) TEM image of the Bi₁₉Br₃S₂₇.

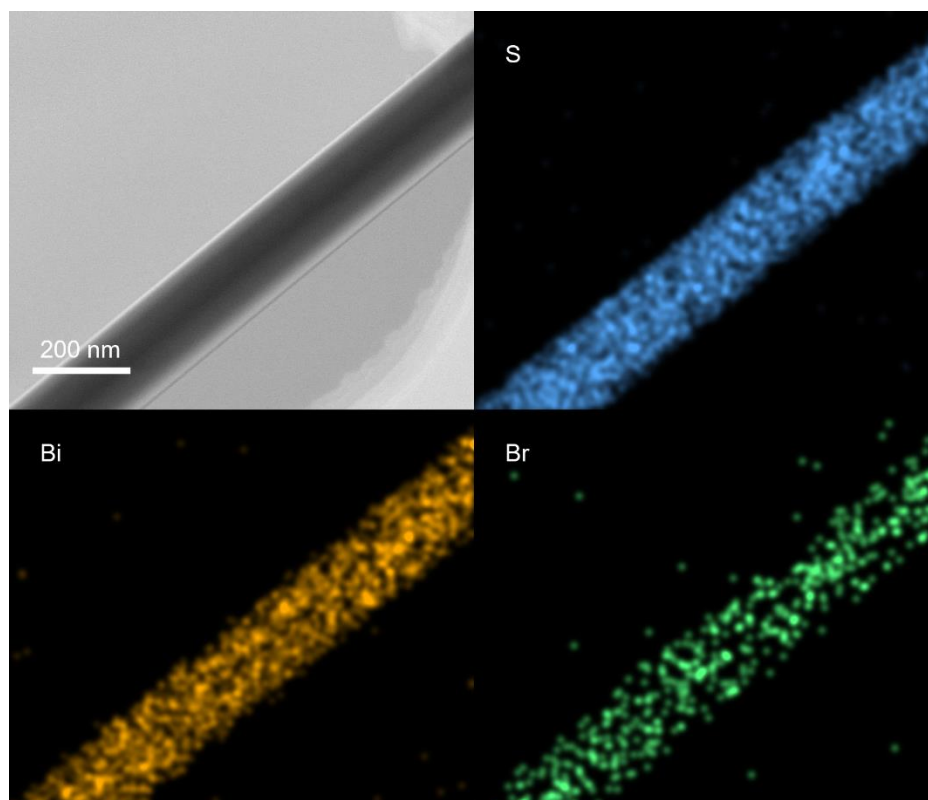


Figure S3 TEM image and EDS elemental mappings of $\text{Bi}_{19}\text{Br}_3\text{S}_{27}$.

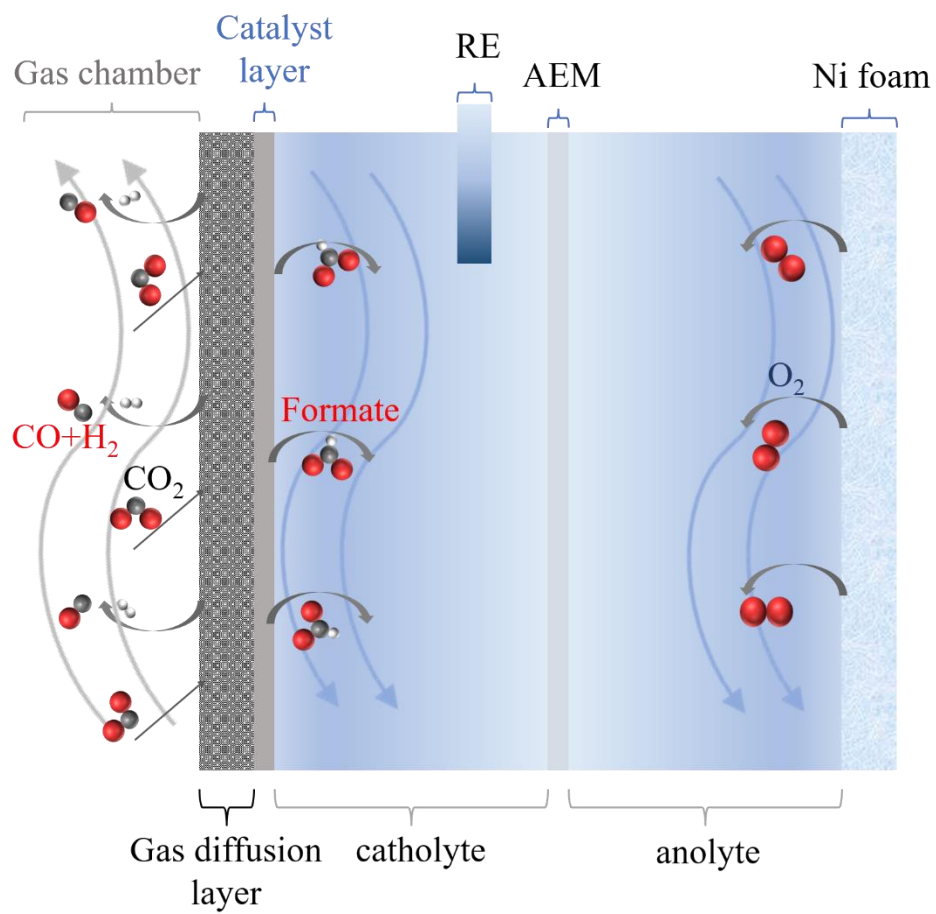


Figure S4 Schematic illustration of the Flow cell.

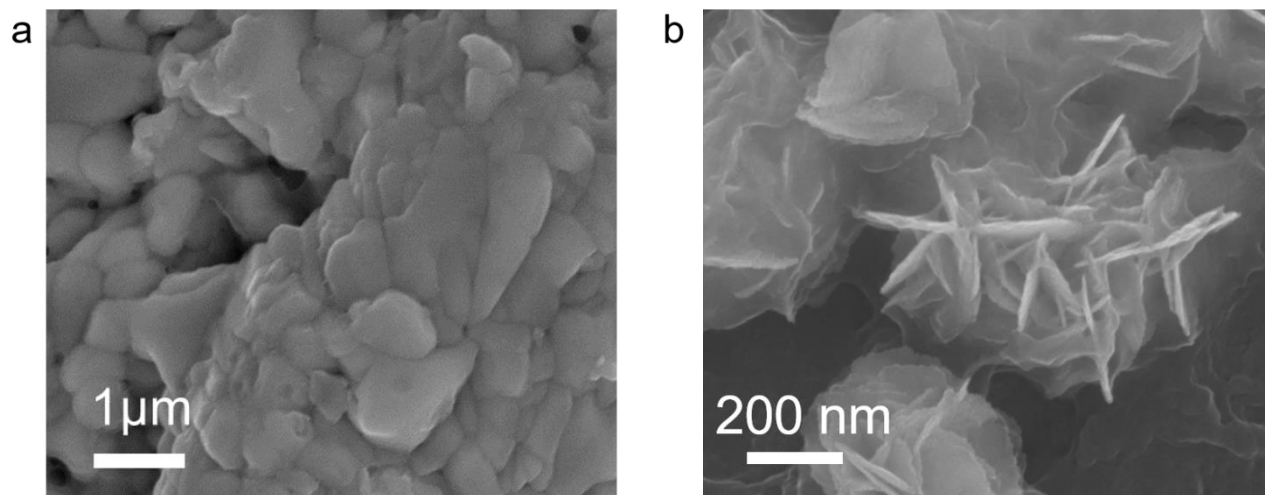


Figure S5 SEM images of Bi (a) and Bi after ECO₂RR (b).

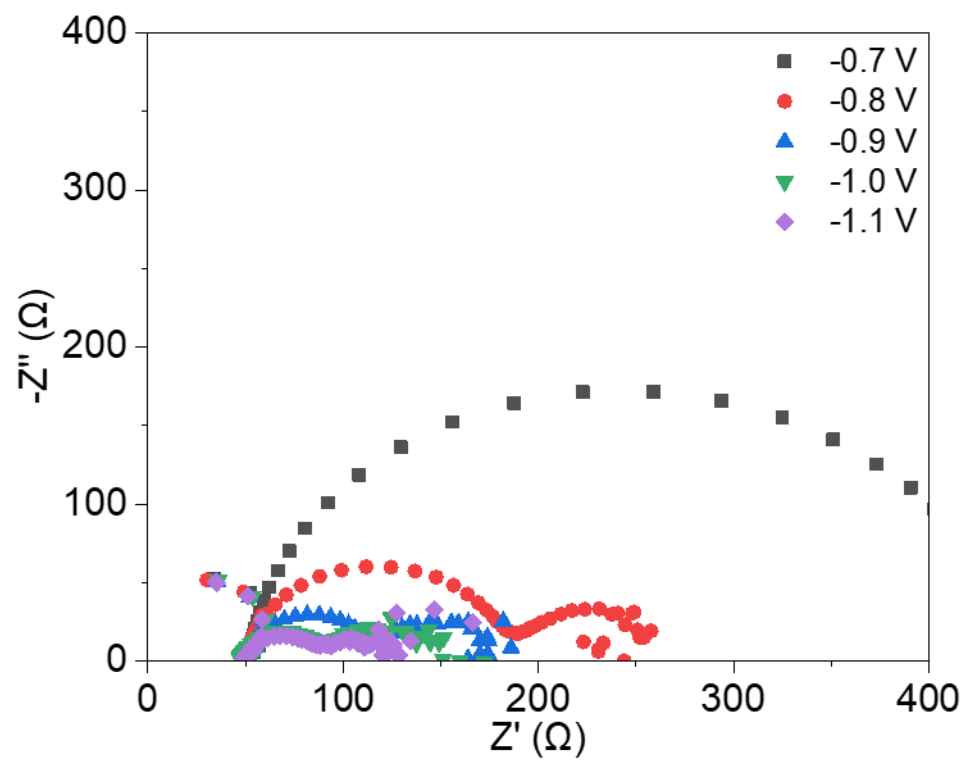


Figure S6 EIS spectra of $\text{Bi}_{19}\text{Br}_3\text{S}_{27}$.

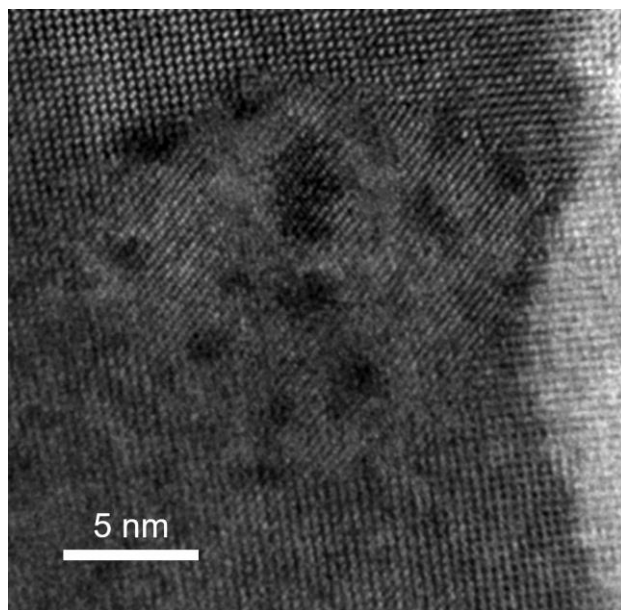


Figure S7 HRTEM image of the BBS catalyst after chronoamperometry.

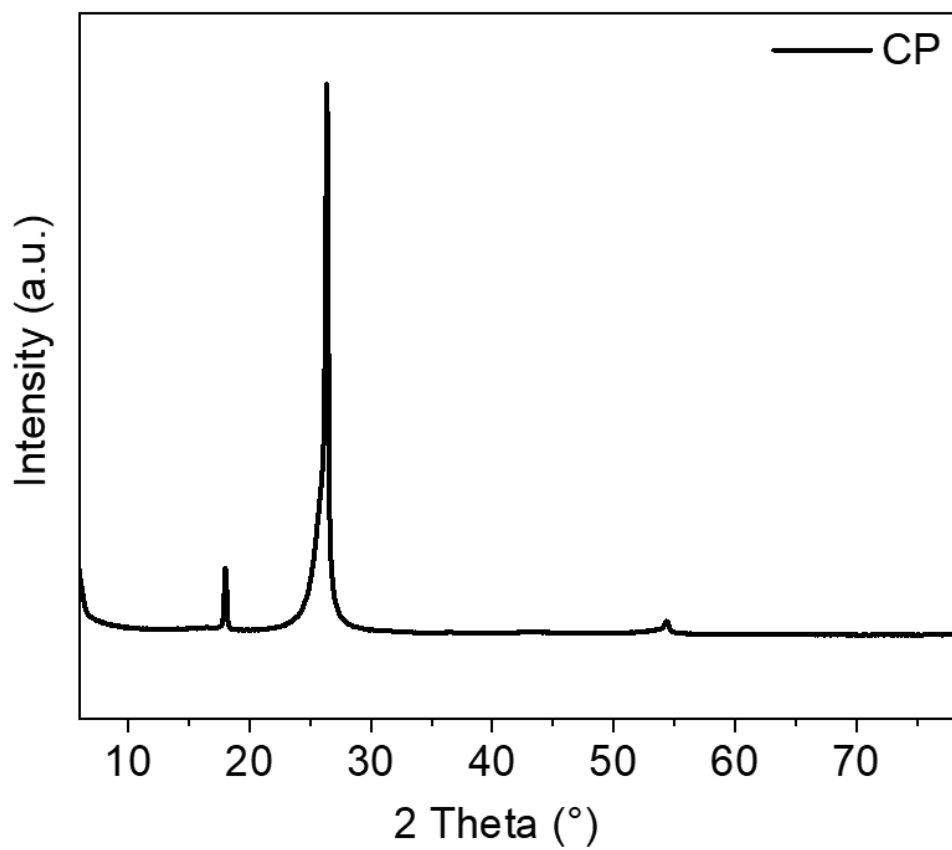


Figure S8 XRD pattern of the carbon paper.

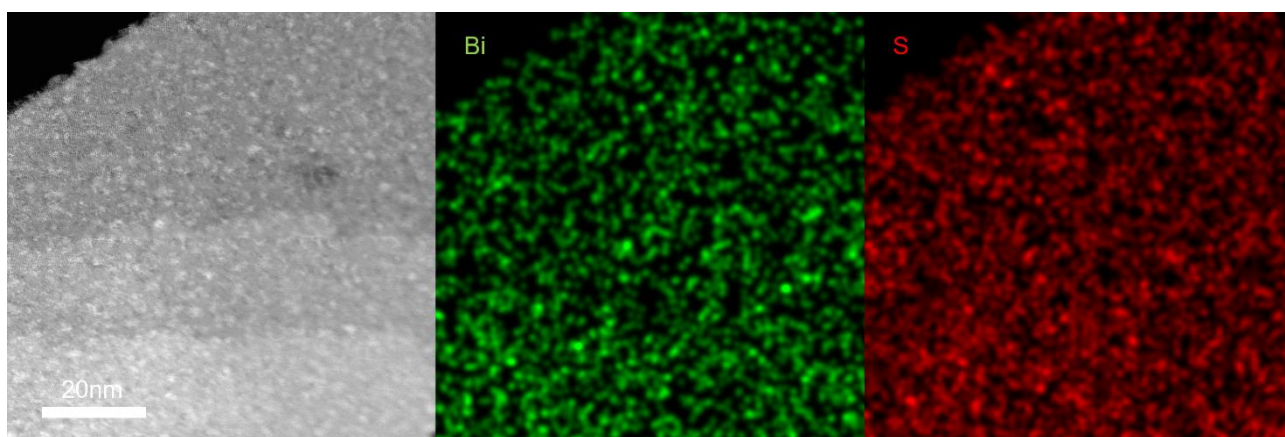


Figure S9 TEM image and EDS mapping of the BBS after ECO₂RR.

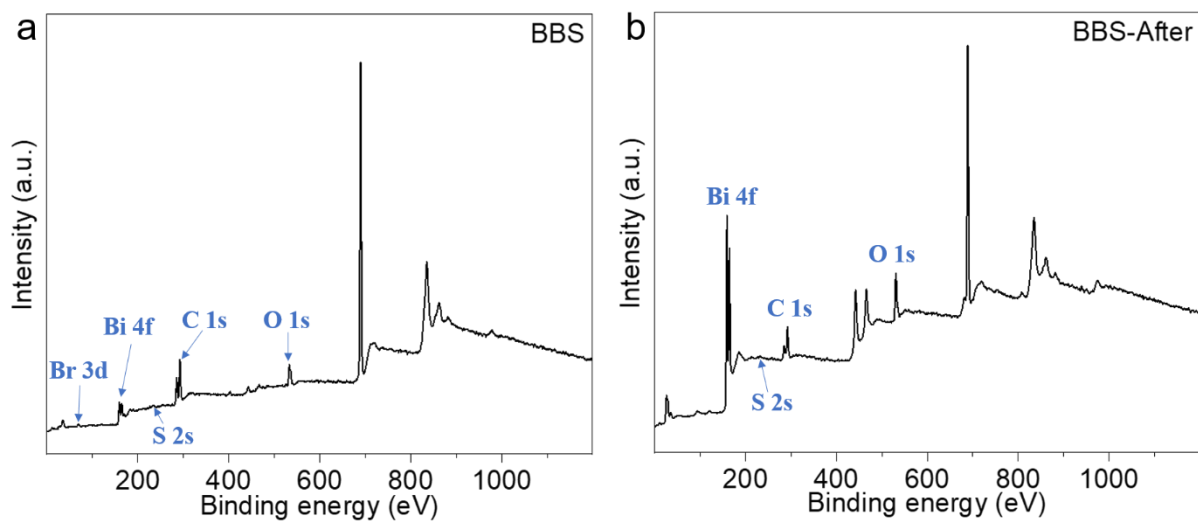


Figure S10 XPS survey spectra of BBS (a) and BBS-after (b).

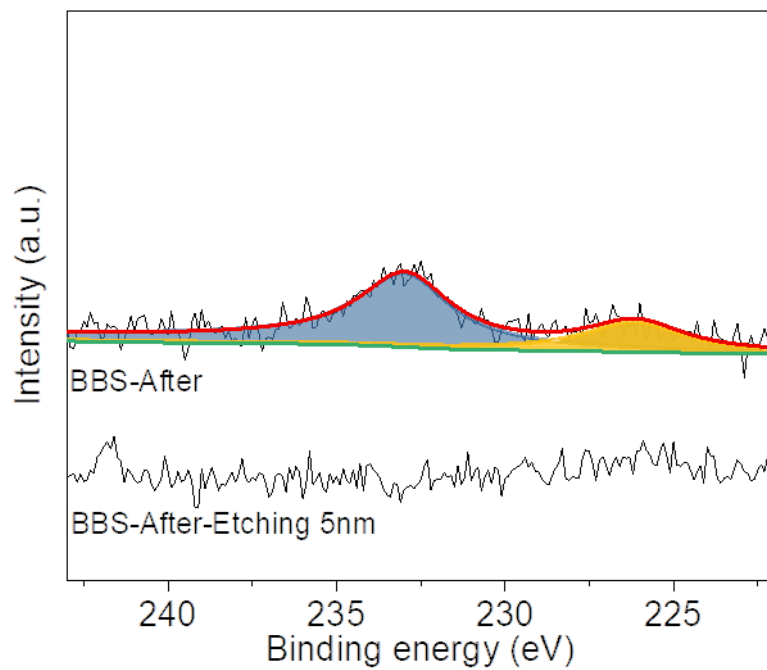


Figure S11 *Ex-situ* S 2s XPS spectra of BSS after chronoamperometry test in 0.5 M KHCO₃ and Etching 5 nm.

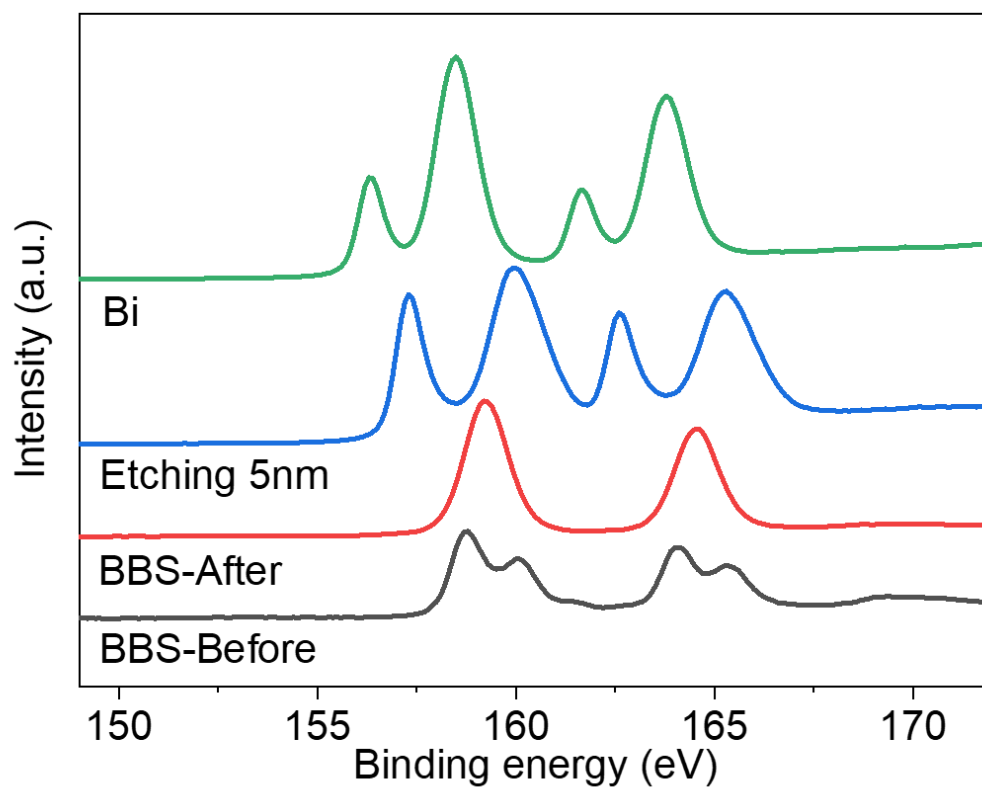


Figure S12 *Ex-situ* Bi 4f XPS spectra of original BBS and that after chronoamperometry test.

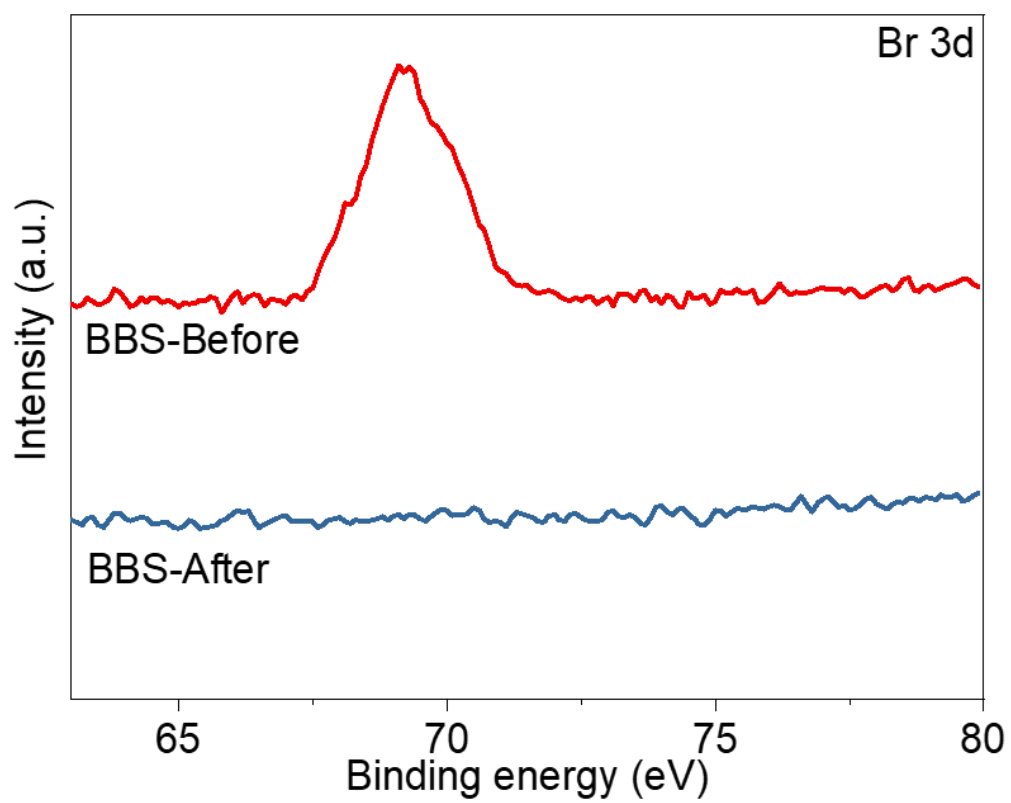


Figure S13 *Ex-situ* Br 3d XPS spectra of original BBS and that after chronoamperometry test.

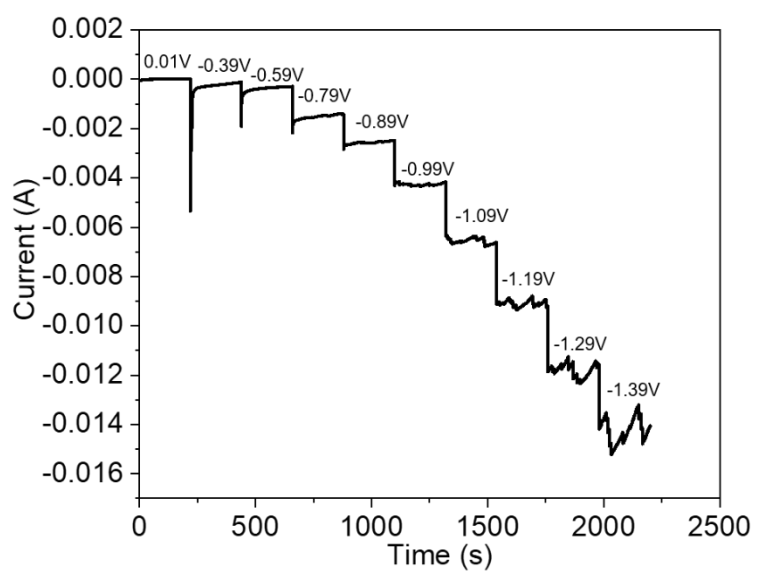
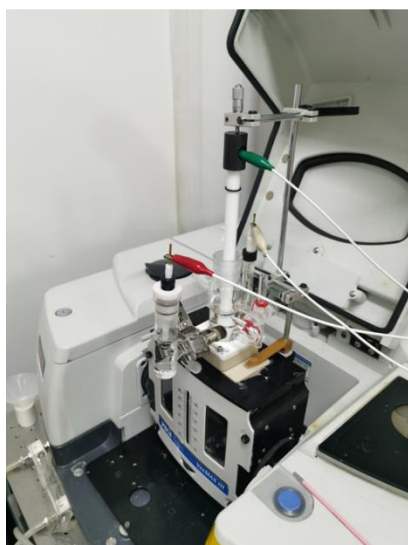


Figure S14 Multi-chronoamperometry test for *in-situ* ATR-SEIRAS test.

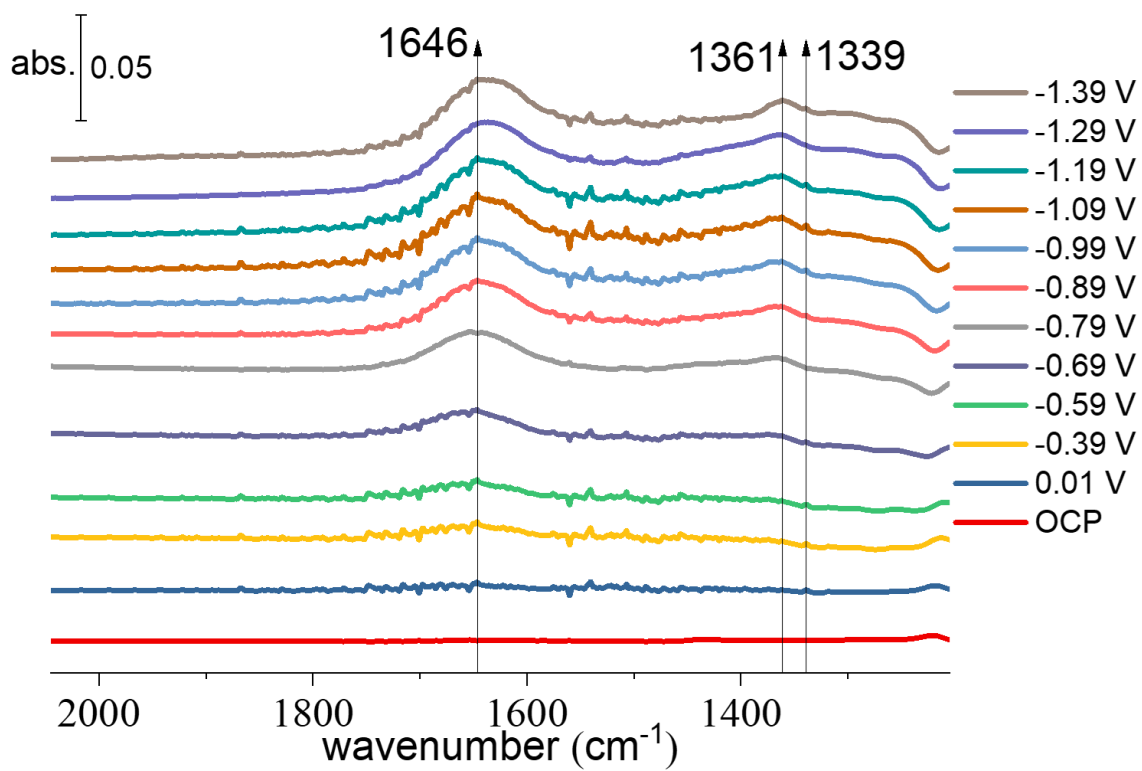


Figure S15 *In-situ* ATR-SERIES spectra of $\text{Bi}_{19}\text{Br}_3\text{S}_{27}$ at different applied potential.

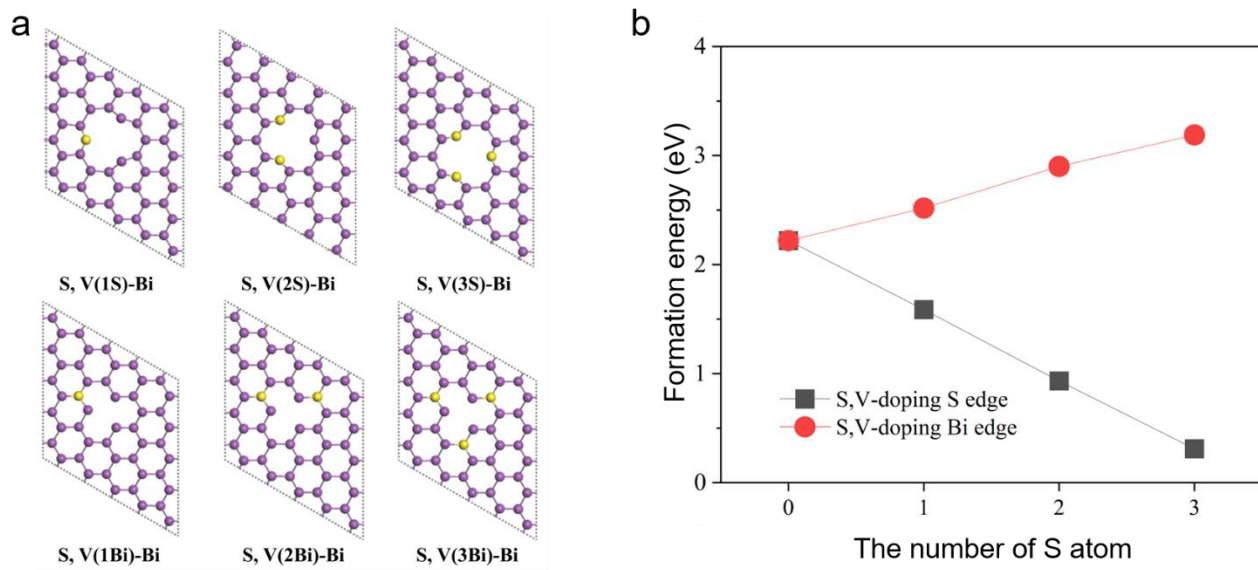


Figure S16 (a) Model diagram of different edge S number. (b) Diagram of the relationship between edge S number and formation energy