Supporting Inforamtion

In situ reconstructing thermally treated Bi_2S_3 nanorods in H_2 followed by O_2 enhances CO_2 electroreduction[†]

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Catalyst Preparation

Synthesis of Bi₂S₃

To prepare Bi_2S_3 , 4 mmol of bismuth nitrate ($Bi(NO_3)_3$) and 6 mmol of thioacetamide were each dissolved in 35 mL of ethylene glycol. After complete dissolution, the two solutions were mixed and stirred for 30 minutes. The resulting mixture was transferred into a hydrothermal reactor and maintained at 180°C for 24 hours. Upon completion of the reaction, the product was centrifuged and washed three times with ethanol. Finally, the material was dried to obtain Bi_2S_3 .

Synthesis of H-Bi₂S₃

For H-Bi₂S₃ preparation, 50 mg of Bi₂S₃ was placed in a quartz boat and subjected to a 10% H₂/N₂ atmosphere in a tube furnace. The temperature was increased at a rate of 5°C/min to 400°C and held for 2 hours. After cooling to room temperature, the H-Bi₂S₃ was obtained.

Synthesis of H/O-Bi₂S₃

For H/O-Bi₂S₃ preparation, 50 mg of Bi₂S₃ was placed in a quartz boat and first reduced under a 10% H₂/N₂ atmosphere in a tube furnace. The temperature was increased at a rate of 5°C/min to 400°C and held for 2 hours. After cooling to room temperature, the H₂ flow was stopped, and the system was purged with N₂ for 30 minutes. Subsequently, a 10% O_2/N_2 atmosphere was introduced, and the temperature was increased at a rate of 5°C/min to 500°C and held for 2 hours. After cooling to room temperature, the H/O-Bi₂S₃ was obtained.

Fabrication of Working Electrode

To fabricate the working electrode, 5 mg of the catalyst was dispersed in a mixed solution of 100 μ L isopropanol, 300 μ L deionized water, and 10 μ L of 5 wt% Nafion solution to prepare a catalyst ink. The solution was ultrasonicated for 1 hour. Then, 80 μ L of the ink was drop-cast onto a 1 × 1.5 cm carbon paper (HCP030P) and dried to obtain the working electrode. The effective coating area was 1 cm², with a catalyst loading of 1.0 mg/cm².

Electrochemical Measurements

All electrochemical measurements were carried out using an electrochemical workstation (CHI660E) in an H-cell configuration. The cathodic and anodic compartments of the H-cell were separated by a Nafion 117 proton exchange membrane, which was pretreated before use. The pretreatment involved immersing the membrane in 5 wt% H_2O_2 at 80°C for 1 hour, followed by soaking in deionized water for 0.5 hour. Next, the membrane was treated with 0.5 M H_2SO_4 at 80°C for 1 hour and finally soaked in deionized water for another 0.5 hours. The electrolyte used in both compartments was 40 mL of 0.5 M KHCO₃.

The reference electrode was Ag/AgCl (saturated KCl), the counter electrode was a carbon rod, and the working electrode was the catalyst-coated carbon paper. All potentials were converted to the reversible hydrogen electrode (RHE) scale using the following equation: $E(V \text{ vs. RHE}) = E(V \text{ vs. Ag/AgCl}) + 0.0591 \times pH + 0.197$. Before performance testing, the H-cell was purged with 15 mL/min of Ar or CO₂ to saturation. Catalyst activation and reconstruction were conducted by cyclic voltammetry (CV) in the potential range of 0 to -1.0 V vs. RHE until the curves stabilized. Linear sweep voltammetry (LSV) was subsequently performed in the same potential range, with a scan rate of 5 mV/s.

The electrochemical active surface area (ECSA) of the catalysts was estimated by measuring the double-layer capacitance (CdI) using CV in a non-Faradaic region (from -0.16 V to -0.04 V vs. RHE). Electrochemical impedance spectroscopy (EIS) was performed by applying an AC voltage of 10 mV amplitude over a frequency range of 10⁵ Hz to 10⁻¹ Hz.

Product Analysis

 CO_2 was purged into the cathodic compartment at a flow rate of 15 mL/min until saturation. Potentiostatic measurements (i-t curves) were conducted at different applied potentials. Gas products, CO and H₂, were analyzed using gas chromatography (GC9790) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Liquid products were analyzed using proton nuclear magnetic resonance (¹H NMR) with dimethyl sulfoxide (DMSO) as the internal standard.

The Tafel slope for CO₂RR was calculated as follows:

 $\eta = blog J_{formate}$

η: overpotential (mV); b: Tafel slope (mV·dec⁻¹); j_{formate}: current density (mA·cm⁻²).

Characterization of catalysts

X-ray diffraction (XRD) was performed by Rigaku Corporation SmartLab 9 operated at 40 kV and 40 mA with Cu Kα radiation. Scanning electron microscope (SEM) were taken by NOVA Nano SEM 450. The energy-dispersive X-ray spectroscopy (EDS) mapping and transmission electron microscopy (TEM) were carried out on JEOL-2100F FETEM operating at 80 kV. X-ray photoelectron spectroscopy (XPS) was obtained using a ESCALAB 250Xi XPS system equipped with AI Ka X-ray source. The hydrophilicity/hydrophobicity of the catalyst was determined by a contact angle measuring instrument (JCD2000D2W). The electron paramagnetic resonance (EPR) spectra were obtained on an EPR spectrometer (A200-9.5/12). The content of S in H/O-Bi₂S₃ was determined by a high-frequency infrared carbon sulfur analyzer (CS-8800, Wuxi Jinyibo Instrument Technology Co., Ltd.), and the S weight content is 1.19wt%.



Figure S1. The XRD patterns of Bi_2S_3 (a), H- Bi_2S_3 (b) and H/O- Bi_2S_3 (c).



Figure S2. TEM images of Bi_2S_3 (a), H- Bi_2S_3 (c) and H/O- Bi_2S_3 (d). SEM image of H- Bi_2S_3 (b).



Figure S3. HRTEM image of $H-Bi_2S_3$.



Figure S4. EDS mappings of ${\rm Bi}_2 S_3$ (a), ${\rm H}\text{-}{\rm Bi}_2 S_3$ (b) and ${\rm H}\text{/}{\rm O}\text{-}{\rm Bi}_2 S_3$ (c).



Figure S5. The XPS survey spectra of Bi_2S_3 , H- Bi_2S_3 and H/O- Bi_2S_3 .



Figure S6. Bi 4f XPS spectrum of H-Bi₂S₃.



Figure S7. S 2s XPS spectra of Bi_2S_3 , H- Bi_2S_3 and H/O- Bi_2S_3 .

As shown in Fig. S7, In the S 2s spectrum of Bi_2S_3 , two peak positions can be observed: one located at 225.1 eV corresponding to the Bi-S bond and another at 231.9 eV attributed to $SO_4^{2^-}$. The presence of $SO_4^{2^-}$ in Bi_2S_3 is due to surface oxidation. After H₂ heat treatment of Bi_2S_3 , the Bi-S bond disappears, and peaks at 228.2 eV corresponding to elemental S and $SO_4^{2^-}$ formed by surface oxidation appear. Further O₂ treatment results in the disappearance of the elemental S peak and the formation of $SO_4^{2^-}$, with the peak intensity of $SO_4^{2^-}$ being significantly higher than that of $SO_4^{2^-}$ formed by surface oxidation. Therefore, during the entire H₂/O₂ heat treatment process, S undergoes a transformation from Bi-S species to elemental S and finally to $SO_4^{2^-}$.





Figure S9. GC of the gas-phase products (a). ¹H NMR spectrum of the electrolytes after electrocatalytic CO₂RR (b) .



Figure S10. Production rate of formate at various potentials over Bi_2S_3 , H- Bi_2S_3 and H/O- Bi_2S_3 .



Figure S11. XRD patterns before and after long term stability of H/O-Bi $_2$ S $_3$ -CV.



Figure S12. CV curves of Bi₂S₃ (a), H-Bi₂S₃ (b) and H/O-Bi₂S₃ (c) under different scan rates from 10 to 120 mV·s⁻¹.



Figure S13. Nyquist plots of Bi_2S_3 , H- Bi_2S_3 and H/O- Bi_2S_3 .



Figure S14. XRD pattern of H-Bi₂S₃-CV.



Figure S15. Bi 4f XPS spectrum of H/O-Bi₂S₃-CV.



Figure S16. (a) LSV curves in Ar or CO₂-saturated 0.5 M KHCO₃ solutions at a scan rate of 5 mV·s⁻¹ of H-Bi₂S₃, H/O-Bi₂S₃ and Bi₂O₃.





Figure S18. LSV curves in Ar or CO₂-saturated 0.5 M KHCO₃ solution with a scan rate of 5 mV s⁻¹ of Bi_2S_3 at different reduction temperatures and the same oxidation temperature.



Figure S19. XRD pattens of the H/O-Bi₂S₃ prepared at different temperatures for thermal treatment of Bi₂S₃ nanorods (T_{TH}) in H₂ followed by O₂ at 500 °C. (a) T_{TH} =350 °C; (b) T_{TH} =500 °C.



Figure S20. XRD pattens of the H/O-Bi₂S₃-CV prepared at different temperatures for thermal treatment of Bi₂S₃ nanorods (T_{TH}) in H₂ followed by O₂ at 500 °C. (a) T_{TH} =350 °C; (b) T_{TH} =500 °C.



Figure S21. O 1s XPS spectra of the H/O-Bi₂S₃-CV prepared at different temperatures for thermal treatment of Bi₂S₃ nanorods (T_{TH}) in H₂ followed by O₂ at 500 °C. (a) T_{TH} =350 °C; (b) T_{TH} =500 °C.



Figure S22. The contact angles of $Bi_2S_3\mbox{-}CV$ (a), $H\mbox{-}Bi_2S_3\mbox{-}CV$ (b) and $H\mbox{/}O\mbox{-}Bi_2S_3\mbox{-}CV$ (c).

Catalysts	E (V vs RHE)	Current densityª (mA⋅cm⁻²)	FE _{formate(} %)	Electrolyte ^b	Ref.
Bi ₂ O ₃ @C-800	-0.9	8.2	92	0.5M KHCO ₃	[1]
PD-Bi1	-0.9	8.75	91.4	0.5 M KHCO_3	[2]
Bi ₂ O ₃ NSs@MCCM	-1.256	15.9	93.8	0.1 M KHCO ₃	[3]
Bi ₂ S ₃ -PPy	-0.9	15.0	91.2	0.5 M KHCO_3	[4]
Bi-CrOx	-0.8	10.0	94.4	0.5 M KHCO_3	[5]
Bi ₄ O ₇ /S	-0.8	9.8	91.2	0.5M KHCO ₃	[6]
Bi-NFs	-0.9	12.3	92.3	0.1M KHCO ₃	[7]
Bi NS	-1.1	10.8	92.0	0.5 M KHCO_3	[8]
CT/h-BiOBr	-0.9	18.4	98.0	0.5 M KHCO_3	[9]
Bi NS	-1.07	30	80	0.5 M KHCO_3	[10]
Bi-SnO _x	-0.88	20.0	95.8	0.5 M KHCO_3	[11]
f-Bi ₂ O ₃	-1.2	24.0	80	0.1M KHCO ₃	[12]
Bi-DC	-1.06	15	95.7	0.1M KHCO ₃	[13]
Bi-TA	-1.1	25	~96	0.5 M KHCO_3	[14]
Bi/CeOx	-1.0	14.8	94.5	0.2 M Na ₂ SO ₄	[15]
Bismuth oxygen clusters	-1.3		82.6	0.5 M KHCO ₃	[16]
Bi–O–S	-0.9	32.8	99.6	0.5 M KHCO_3	[17]
H/O-Bi ₂ S ₃	-0.9	24.8	97.2	0.5 M KHCO_3	This work
H/O-Bi ₂ S ₃	-0.75	4.3	97.7	0.5 M KHCO_3	This work
H/O-Bi ₂ S ₃	-1.0	45.9	95.6	0.5 M KHCO_3	This work

Table S1. Electrocatalytic CO_2 reduction performance of the catalysts in the H-type cell.

^a Total current density. ^b CO₂ saturated solution as electrolyte.

Table S2.

The quantitative results of the O 1s XPS spectra of the H/O-Bi₂S₃-CV prepared at different temperatures for thermal treatment of Bi₂S₃ nanorods (T_{TH}) in H₂ followed by O₂ at 500 °C.

T _{TH}	Surface O ^[a]	Surface Ov	Lattice O	Molar percentage (%)		
	(%)	(%)	(%)	Lattice O	Ov	Adsorbed O
350	28.2	11.1	9.3	32.9	39.3	27.8
400	32.6	21.1	10.7	32.9	64.2	2.9
500	35.4	22.3	5.7	16.0	63.1	20.9

^[a] Oxygen atomic percentage in the samples.

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