Electronic Supplementary Information for

A reconstructed, surface S-coordinated gas-penetrable Cd hollow fiber for selective CO₂ electroreduction to CO at high current density

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1. Experimental

1.1 Chemicals and materials

All chemicals were used as received without further purification. Cd powder (99.9%, 1~3 µm) was purchased from Beijing Gaoke New Material Technology Co., Ltd. Polyethersulfone (PES) was purchased from Jiangsu Suyuan Chemical Trade Co., Ltd. N-methyl-2-pyrrolidone (NMP, \geq 99.0%) and potassium bicarbonate (KHCO₃, \geq 99.5%) was purchased from Shanghai Titan Scientific Co., Ltd. Thioacetamide (C₂H₅NS, \geq 99.0%) was purchased from Sinopharm Chemical Reagent Co., Ltd. Ethylrnrdiamine (C₂H₈N₂, \geq 99.0%) was purchased from Yantai Shuangshuang Chemical Co., Ltd. Anhydrous ethanol (C₂H₅OH, \geq 99.7%) was purchased from Tianjin Damao Co., Ltd. The high-purity carbon dioxide (CO₂, 99.999%) and nitrogen (N₂, 99.999%) was purchased from Jinghua Industrial Gas Co., Ltd. Nafion 117 membrane was purchased from by Alfa Aesar Chemical Co., Ltd. Ultrapure water (18.2 M Ω cm) was obtained from a water purification system (Hitech ECO-S20).

1.2 Catalysts preparation

1.2.1 Fabrication of CdO hollow fiber (CdO HF)

CdO HF was fabricated according to a previously reported combined phaseinversion/sintering process.¹ In brief, 10 g of PES (10 wt%) was first added into 40 g of NMP (40 wt%) and the resulting mixture was heated at 80 °C for 30 min to obtain a transparent solution, to which 50 g of Cd powder (50 wt%, 1~3 μ m) was then added. Afterward, the as-obtained slurry was transferred into a ball-milling tank (zirconia, 100 mL) filled with 40 g of zirconia balls and ball-milled 300 rpm for 3 h to form a homogeneous slurry. After cooling to room temperature, the slurry was vacuumized (1 mbar) for 12 h to remove the bubbles to obtain a casting solution. Subsequently, the casting solution was extruded through a spinning machine and shaped in a water bath *via* the phase-inversion process. After spinning, the as-formed microtubes were kept in a water bath for 24 h to eliminate the NMP followed by stretching and drying for 48 h to obtain the Cd HF precursor. The Cd HF precursor was cut into 6 cm in length and then calcinated in an air flow (100 mL min⁻¹) at 300 °C (heating rate: 1 °C min⁻¹) for 3 h to partially oxidize the Cd HF precursor. Subsequently, the tube furnace was directly heated to 600 °C (heating rate: 2 °C min⁻¹) for 5 h in an air flow (100 mL min⁻¹) to obtain CdO HF. (Note: *Cd is a highly toxic element. When exposed to Cd metal, it is necessary to wear a respiratory protective mask, goggles, protective gloves, and experimental clothing, and pay attention to personnel protection.*)

1.2.2 Fabrication of Cd HF

Cd HF was prepared by *in-situ* electrochemically reducing CdO HF in a CO_2 satruraed 0.5 M KHCO₃ solution. The CdO HF was first stuck into a Cu tube using conductive silver adhesive for electrical contact, while the end of the CdO HF as well as the joints between the CdO HF and Cu tube were sealed with nonconductive epoxy. After drying at room temperature for 1 h, the CdO HF working electrode was directly used for the CO₂RR, during which CdO HF was *in situ* electrochemically reduced into Cd HF.

1.2.3 Fabrication of s-Cd HF

To prepare s-Cd HF, the CdO HF was first converted into CdS@CdO HF via the hydrothermal sulfurization reaction. In brief, CdO HF was transferred into a 100 mL of Teflon-lined stainless-steel autoclave containing 60 mL of C_2H_5NS (48 mM) and $C_2H_8N_2$ (25 mM) and heated at various temperature (150 °C, 180 °C, 210 °C, and 240 °C) for 2 h. The obtained CdS@CdO HF was rinsed with distilled water and ethanol and dried in a vacuum oven at 60 °C for 8 h. Then, the as-obtained CdS@CdO HF was engineered into a GPE and directly used for the CO₂RR using the exact same

procedures for the preparation of Cd HF, during which the CdS@CdO HF was *in situ* electrochemically reduced to obtain s-Cd HF.

1.3 Characterization

X-ray diffraction (XRD) patterns were analyzed in the 2θ range of 5~80° with a scanning rate of 10° min⁻¹ using a Rigaku Smartlab diffractometer with Cu K α radiation, operating at 40 kV and 40 mA. Scanning electron microscopy (SEM) images and energy X-ray spectrometer (EDX) were taken with a SIGMA 500 scanning electron microscope. Transmission electron microscopy (TEM) images were taken with a FEI Talos 200S field emission transmission electron microscope. X-ray photoelectron spectroscopy (XPS) measurements of the samples were performed on a Thermo Fisher Escalab-250Xi electron spectrometer using an Al K α X-ray source. All spectra were calibrated according to the C 1s binding energy at 284.8 eV.

1.4 CO₂ gas permeability measurements

The CO₂ gas permeability of the CdO HF and CdS@CdO HF was measured with a custom gas permeability device (Fig. S1). The gas permeability of the CdO HF and CdS@CdO HF was calculated based on the measured gas flux and pressure drop using Equation (1):

$$P = \frac{F}{A \times \Delta p} \qquad (1)$$

where *P* is the gas permeability (mol m⁻² pa⁻¹ s⁻¹), *F* is the molar flow rate (mol s⁻¹), A is the CdO HF and CdS@CdO HF outer surface area (m²), and Δp is the pressure drop (pa) across the HFs. *P* was reported in GPU and 1 GPU= 3.35×10^{-10} mol m⁻² pa⁻¹ s⁻¹.

1.5 Electrical conductivity measurements

The conductivity of the HF was calculated based on the measured length of the HF and electrical resistances using Equation (2):

$$\delta = \frac{L}{R \times S} \qquad (2)$$

where δ is the conductivity (S m⁻¹), *L* is the length of CdO HF between two probes (m), *R* is the resistance (Ω), *S* is the cross-sectional area of the HF (m²).

1.6 Electrocatalytic CO₂ reduction experiments

All the electrochemical experiments were conducted in an H-type electrochemical cell separated by a Nafion 117 membrane with a potentiostat (CS350M; Corrtest Instruments). A Pt mesh and a saturated Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. A 0.5 M KHCO₃ solution was used as the supporting electrolyte. The working electrode was prepared by stuncking HF tube (CdO HF and CdS@CdO HF) into a Cu tube using conductive silver adhesive, while the end of the HF tube as well as the joints between the HF tube and Cu tube were sealed with nonconductive epoxy. The Cu tube was then connected to one inlet for gas flow in at a rate of 30 mL min⁻¹. Liner sweep voltammetry (LSV) measurements were carried out in N₂- or CO₂-saturated 0.5 M KHCO₃ solution at a scan rate of 10 mV s⁻¹. Electrical double layer capacitances of the electrodes were determined by performing cyclic voltammetry (CV) measurements in a non-faradaic region (0.31~0.41 V) in N₂ bubbling 0.5 M KHCO₃ solution. The electrochemical impedance spectroscopy (EIS) measurements were performed at the open circuit potential (-0.85 V vs. Ag/AgCl) in a frequency range from 0.01 Hz to 100 kHz with a voltage amplitude of 5 mV. Prior to EIS measurements, the HFs were electrochemically reduced at a constant potential of -2.2 V vs. Ag/AgCl for 1 h. All the applied potentials were recorded against the saturated Ag/AgCl reference electrode and then converted to those versus the reversible hydrogen electrode (RHE) with iR_s corrections by the following equation (3):

$$E(vs. RHE) = E(vs. Ag/AgCl) + 0.197 V + 0.059 V \times pH + iRs$$
 (3)

where E (vs. Ag/AgCl) is the applied potential, pH is the pondus hydrogenii value of

the CO₂-saturated 0.5 M KHCO₃ solution (~7.8), *i* is the current density at each applied potential, and R_s is the solution resistance obtained by EIS measurements.

For the bulk CO₂ electrolysis, the flow rate of the CO₂ gas varies from 10 to 40 mL min⁻¹, and the gas effluent from the cathodic compartment was delivered directly to the sampling loop of an on-line pre-calibrated gas chromatograph (PANNA GC-A91 plus) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The Faradaic efficiency (FE) for the gaseous products were calculated based on the following Equation (4):

$$FE_{i} (\%) = \frac{Z_{i} \times G \times V_{i} \times t \times p_{0} \times F \times 10^{-3}}{Q_{\text{total}} \times R \times T_{0}} \times 100\%$$
(4)

where Z is the number of electrons transferred; G is volumetric outlet flow rate; V_i is the volume ratio of gas product i; t is reaction time (min); and p_0 is the atmospheric pressure (101.3 kPa), T_0 is the reaction temperature (298.15 K), F is faradaic constant (96485 C mol⁻¹), Q_{total} is integrated charge at each applied potential and R is ideal gas constant (8.314 J·mol⁻¹ K⁻¹).

The liquid products were collected at the end of the electrolysis and analyzed using an ion chromatograph (IC, Dionex Aquion) and a high-performance liquid chromatography (HPLC, Hitachi) system equipped with C18 column and UV detector.

2. Additional data



Fig. S1 The diagram of the gas permeability testing system.



Fig. S2 (a) XRD pattern of the CdO HF. (b) Survey, (c) Cd 3d, and (d) O 1s XPS spectra of CdO HF.



Fig. S3 SEM images of (a) cross-section, (b-d) outer surface, and (e-g) inner surface



of CdO HF.

Fig. S4 (a) CO₂ gas permeability of CdO HF at different CO₂ flow rates. 1

GPU= 3.35×10^{-10} mol m⁻² pa⁻¹ s⁻¹. (b) Electrical conductivity of CdO HF. The length of the CdO HF between two probes is 2 cm and the measured resistance of CdO HF is 35.8 Ω. The conductivity of CdO HF was then calculated to be 641.4 S m⁻¹.



Fig. S5 SEM images of (a) cross-section, (b-d) inner surface and (e-g) outer surface of



Cd HF.

Fig. S6 (a) XRD pattern of Cd HF. (b) Survey, (c) Cd 3d, and (d) O 1s XPS spectra of Cd HF.



Fig. S7 Optical photos of CdO HF and CdS@CdO HF.



Fig. S8 XRD pattern of CdS@CdO HF.



Fig. S9 SEM images of inner surface of CdS@CdO HF.



Fig. S10 CO₂ gas permeability of CdS@CdO HF at different CO₂ flow rates. 1

GPU= $3.35 \times 10^{-10} \text{ mol m}^{-2} \text{ pa}^{-1} \text{ s}^{-1}$.



Fig. S11 SEM images showing the morphology evolution of grown CdS particles on CdS@CdO HF with the hydrothermal temperature.



Fig. S12 XRD pattern of s-Cd HF.



Fig. S13 SEM images of inner surface of s-Cd HF.



Fig. S14 FE_{CO} and j_{CO} for s-Cd HF prepared at different hydrothermal temperatures.



Fig. S15 CV curves of (a) Cd HF and (b) s-Cd HF in the non-Faradaic region at

different scan rates.



Fig. S16 ECSA-normalized partial current densities of CO production for Cd HF and

s-Cd HF.



Fig. S17 SEM images of (a) cross-section, (b and c) outer surface of s-Cd HF after

CO₂RR stability test.



Fig. S18 (a) Survey XPS spectrum, (b) content and relative ratio of the Cd, S, and O elements (the main residual element in the materials is contaminated carbon, which is omitted for clarity), (c) S 2p, and (d) Cd 3d XPS spectra of s-Cd HF after CO₂RR stability test.



Fig. S19 FE_{CO} and j_{CO} of s-Cd HF at -0.96 V vs. RHE with different CO₂ flow rates.

Catalyst	Reactor	Electrolyte	Potential (V vs. RHE)	FE _{CO} (%)	$j_{\rm CO}$ (mA cm ⁻²)	Ref	
CdS _x Se _{1-x}	H-type cell	0.1 M KHCO ₃	-1.20	81.0	-22.0	2	
CdS-CNTs	H-type cell	0.1 M KHCO ₃	-1.20	92.0	-11.4	3	
Ag-CdS _{1-x}	H-type cell	1 M KHCO ₃	-1.10	87.1	-46.8	4	
$Au_{19}Cd_2$	H-type cell	0.5 M KHCO ₃	-0.90	95.0	-40	5	
$Au_{47}Cd_2(TBBT)_{31}$	H-type cell	0.5 M KHCO ₃	-0.90	80.0	-8	6	
Cd-NC-5M SACs	H-type cell	0.5 M KHCO ₃	-0.73	91.4	-5.3	7	
Cd-BDC MOFs	H-type cell Flow cell	0.1 M KHCO ₃ 0.5 M KHCO ₃	-1.00 -1.10	88.9 ~90.0	-2.8 -108.1	8	
Cd/Cd(OH) ₂ /CP	H-type cell	30 wt% [Bmim]PF ₆ -65 wt% CH ₃ CN-5 wt% H ₂ O	-2.00 (Ag/AgCl)	98.3	-23.8	9	
Cu ₂ Cd/Cd/Cu	H-type cell	0.1 M KHCO ₃	-1.00	84.0	-8.0	10	
Cd(OH) ₂	H-type cell	0.5 M [BMIM]PF ₆ /MeCN	-1.85	99.2	-59.0	11	
Cdhy-QS	H-type cell	0.5 M [BMIM]PF ₆ /MeCN	-2.50 (Ag/AgCl)	~100.0	-200.0	12	
CdCO ₃ -CNFs	H-type cell	0.1 M KHCO3	-0.83	93.4	-10.0	13	
CdS nanorods	H-type cell	0.5 M KHCO ₃	-0.90	95.0	-52.3	14	

Table S1 CO₂RR performance comparison of s-Cd HF with other Cd-based electrocatalysts in the H-type cells and flow cells for CO production.

Cd/Zn	H-type cell	30 wt% [Bmim]PF ₆ - MeCN-5 wt% H ₂ O	-2.50 (Ag/AgCl)	99.0	~-15.0	15
Cd-PCN-222HTs	H-type cell	30 wt% [Bmim]PF ₆ -65 wt% CH ₃ CN-5 wt% H ₂ O	-2.40 (Ag/AgCl)	>80%	68.0	16
CdS NNs	H-type cell Flow cell	0.1 M KHCO ₃ 0.1 M KOH	-1.00 -1.20	91.1 95.5	~-11.0 -212.0	17
CdN ₄ S ₁ /CN	H-type cell	0.5 M [BMIM]PF ₆ /MeCN	-2.40 (Ag/AgCl)	99.7	-182.2	18
$Au_{24}Cd_1(PET)_{18}$	H-type cell	1 M KHCO ₃	-0.60	>80%	-18.1	19
s-Cd HF ^a	H-type cell	0.5 M KHCO ₃	-1.01	90.2	-125.1	This work

^{*a*} s-Cd HF was prepared from the CdS@CdO HF obtained *via* the hydrothermal sulfurization of CdO HF at 240 °C.

Catalyst	Electrolyte	Potential (V vs. RHE)	FE _{CO} (%)	$j_{\rm CO}$ (A cm ⁻²)	Ref
CD-Ag HPE	3 M KCl+0.05 M H ₂ SO ₄		95.0	-4.3	20
Cl-Ag HF	3 M KCl	-0.91	92.3	-0.92	21
Ag HF	0.5 M KHCO ₃	-1.2	92	-0.14	22
Cu-Ni HF	0.1 M KHCO ₃	-1.5 (Ag/AgCl)	77.5	-0.014	23
NS@Ag HF	3 M KCl		97	-2.0	24
ZncNS-HF	0.5 M KCl	-1.3	72	-0.058	25
AgZnNS-HF	0.5 M KCl	-1.3	88.6	-0.083	26
Ni HF (Bi@Zeolite)	[Bmim]PF ₆ /MeCN/H ₂ O	-1.8	74.1	-0.005	27
CuSb-3	0.5 M KHCO ₃	-1.0	72	-0.4	28
Cu HF	0.3 M KHCO ₃	-0.4	72	-0.007	29
s-Cd HF	0.5 M KHCO ₃	-1.01	90.2	-0.125	This work

Table S2 Comparison of CO_2RR performance of s-Cd HF with other HF for CO electrosynthesis.

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