Supporting Information for

Ultrathin two-dimensional mesoporous holmium oxide nanosheet stabilized

copper nanoparticle for stable and efficiency electrocatalytic semi-hydrogenation

of acetylene

Huawei Li, Miao He, Senyao Meng, Ping Wang, Cheng Yang, Jiasai Yao, Zikang Hu, and Zhenxing Li*

State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, People's Republic of China

*corresponding author *E-mail address*: lizx@cup.edu.cn (Z. Li).

Experimental Section Preparation of the working electrodes

30 mg of the catalyst precursor powder was dispersed in 4 ml of isopropanol with sonication for 1 h. Then, 100 μ l of Nafion solution (5 wt%) was added into the solution for another 30 min. After that, the precursor ink was airburshed onto a piece of 3×1 cm² carbon paper (YLS-30T) to obtain the working electrode.

Electrochemical measurements

All electrochemical measurements were conducted at room temperature. CHI 1130 electrochemical workstations were employed for the electrochemical measurements. The Ag/AgCl (saturated KCl) was adopted as the reference electrode, and the counter electrode was Ni foam for the oxygen evolution reaction. All potentials were converted to the RHE reference scale using the relation below and the solution resistance was compensated with an 85% compensation coefficient unless otherwise mentioned.

Silicone gaskets with a $0.5 \times 2 \text{ cm}^2$ window at the center were placed between each layer for sealing. The 1.0 M KOH electrolyte was pumped and circulated through both the anode and cathode chambers at a rate of 6 mL/min. Meanwhile, 20% C₂H₂/Ar (25 sccm) was continuously flowed was through void space behind the cathode. **Products analysis**

The gas products $(H_2, C_2H_2, C_2H_4, C_2H_6)$ were analyzed using a gas chromatograph (GC, Beijing General Analysis GC-1100) coupled with a thermal conductivity detector and flame ionization detector. The FE of the gas products was calculated through the concentration (x) detected by GC according to the equation:

$$FE(\%) = \frac{nFxv/(V_m I)}{(1/60)} \times 100\%$$
(2)

where n is the electron transfer number, F is Faraday constant (96,485 C mol⁻¹), x is the mole fraction of the product, v is the flow rate of gas (sccm), V_m is the molar volume (24.5 L mol⁻¹), and I is the applied current (A). FTIR testing Detailed characterization procedure for C₂H₂-adsorption in suit DRIFT

Before C_2H_2 adsorption, a pretreatment was conducted on a 2 mg sample. The catalyst was dissolved in ethanol along with a small amount of Nafion solution, and then dropped onto a silicon crystal. Nitrogen gas was introduced into the infrared device, and the infrared cell was cooled with liquid nitrogen to collect the background spectrum. The catalyst was placed in KOH solution, connected to an electrochemical workstation for C_2H_2 adsorption, and the infrared spectrum of the product was collected. Changing the working current or extending the reaction time, the infrared spectrum of the catalyst is collected.

In situ Raman test details during C2H2-adsorption

The 4mg catalyst was dissolved in ethanol with a small amount of Nafion solution and then dropped on carbon paper with a catalyst density of 1mg cm⁻². The carbon paper is placed in an in-situ Raman spectroelectrochemical cell in which a flowing KOH solution and C_2H_2 gas are passed. An electrochemical workstation was connected for

 C_2H_2 adsorption, and Raman spectra of the products were collected. Change the working current or extend the reaction time to collect the Raman spectrum of the catalyst.

DFT computations

DFT calculation details. The VASP software code to perform spin-polarized density functional theory (DFT) calculations. The ion-electron interactions are described using the projected enhanced wave (PAW) method, and the electron exchange effects and associated energies are approximately solved within the generalized gradient with the Perdew Burke-Ernzerhof form (GGA-PBE). All calculated plane-wave fundamental energy cutoffs were set to 400 eV. The atomic coordinates are completely relaxed until the maximum force on each atom is less than 0.05 eV/Å, and the energy convergence condition is 10⁻⁶ eV. The Cu/Ho₂O₃ composite catalyst was simulated by Cu-Cu bond and Ho-O bond. The Brillouin zone was sampled at Gamma point with the 2×2×1 k-point meshes for all calculations. For all the models, we have set the vacuum space of 16 Å along the z-axis to guarantee sufficient space for geometry relaxation and intermediate adsorptions. All the atoms were allowed to be relaxed during the geometry optimization.



Fig. S1. (a, d, g, j, m) XRD patterns (The peak in the triangular position is the Cu (111) crystal face), (b, e, h, k, n) N_2 adsorption-desorption isotherm, (c, f, i, l, o) Pore size distribution by Cu/rare earth oxide catalysts.



Fig. S2. FE of electrocatalytic semi-hydrogenation of acetylene products at different current density with pure Cu.



Fig. S3. Electrochemical active surface area of Cu/Ho $_2O_3$, Ho $_2O_3$, Cu.



Fig. S4. LSV curves of Cu/Ho $_2O_3$, Ho $_2O_3$, Cu.



Fig. S5. Electrochemical impedance spectra of Cu/Ho $_2O_3$, Ho $_2O_3$, Cu.



Fig. S6. Catalyst stability of Cu/Ho $_2O_3$ at 100 mA cm $^{\text{-2}}$.



Fig. S7. Catalyst stability of pure Cu at 40 mA cm $^{\text{-2}}$.



Fig. S8. (a) Cu K-edge, EXAFS oscillation functions of Cu/Ho₂O₃, Cu foil. (b) Ho L3-edge, EXAFS oscillation functions of Cu/Ho₂O₃, bulk Ho₂O₃.



Fig. S9. Corresponding electrocatalytic semi-hydrogenation of acetylene reaction steps of (a) Cu and (b) Cu/Ho₂O₃. Figure S9 shows the adsorption processes of acetylene electrocatalytic semi-hydrogenation of Cu and Cu/Ho₂O₃, followed by the adsorption of *C₂H₂, *C₂H₂+*H, *C₂H₃, *C₂H₃+*H and *C₂H₄ on Cu, the corresponding energies are shown in Figure 6f.



Fig. S10. (a) TEM image of Cu/Ho_2O_3 . (b) Particle size distribution of Cu nanoparticles in Cu/Ho_2O_3 .



Fig. S11. (a) Cu K-edge XANES profiles for Cu/Ho₂O₃, Cu foil. (b) Ho L3-edge XANES profiles for Cu/Ho₂O₃, bulk Ho_2O_3 .

Other rare earth products	Specific surface area (m ² /g)	Pore size (nm)	
Cu/Y ₂ O ₃	22.85	4.08	
Cu/La ₂ O ₃	21.36	3.92	
Cu/CeO ₂	20.88	3.49	
Cu/Pr ₂ O ₃	23.81	3.88	
Cu/Nd ₂ O ₃	24.81	4.11	
Cu/Sm ₂ O ₃	19.42	3.51	
Cu/Eu ₂ O ₃	20.40	4.00	
Cu/Gd ₂ O ₃	19.58	3.91	
Cu/Tb ₂ O ₃	20.03	4.32	
Cu/Dy ₂ O ₃	18.12	3.98	
Cu/Ho ₂ O ₃	23.75	3.87	
Cu/Er ₂ O ₃	21.17	3.49	
Cu/Tm ₂ O ₃	21.98	3.78	
Cu/Yb ₂ O ₃	22.65	4.07	
Cu/Lu ₂ O ₃	20.39	3.64	

 Table S1. Comparison of specific surface area and pore size by Cu/rare earth oxide catalysts.

Other rare earth products	FE of C ₂ H ₄ (%)	FE of H ₂ (%)	FE of C ₂ H ₆ (%)	
Cu/Y ₂ O ₃	89.18	1.61	0.18	-
Cu/La ₂ O ₃	70.05	0.93	0.67	
Cu/CeO ₂	69.71	2.23	0.17	
Cu/Pr ₂ O ₃	76.40	1.89	0.26	
Cu/Nd ₂ O ₃	84.27	0.86	0.13	
Cu/Sm ₂ O ₃	72.73	2.78	0.12	
Cu/Eu ₂ O ₃	70.85	1.56	0.20	
Cu/Gd ₂ O ₃	80.47	1.85	0.81	
Cu/Tb ₂ O ₃	82.02	0.41	0.14	
Cu/Dy ₂ O ₃	78.48	0.92	0.30	
Cu/Ho ₂ O ₃	95.07	0.28	0.40	
Cu/Er ₂ O ₃	91.88	0.61	0.19	
Cu/Tm ₂ O ₃	90.95	1.23	0.06	
Cu/Yb ₂ O ₃	89.02	0.48	0.12	
Cu/Lu ₂ O ₃	91.57	1.03	0.15	

Table S2. Comparison of FE in ele	ctrocatalytic semi-hydrogenation of	of acetylene by Cu/rare earth oxide cat	alysts.
-----------------------------------	-------------------------------------	---	---------

-1			
Catalyst	Current density (mA cm ⁻²)	C ₂ H ₄ FE (%)	Refs
Cu/Ho ₂ O ₃	60	98.12	This work
LD-Cu	30	68	Ref.4
NHC-Cu	60	66	Ref.5
Cu-SA/TiO ₂	10	83.9	Ref.7
Cu-F	17.5	84.17	Ref.8
Cu dendrites	50	93	Ref.15
Cu-Cd/Zr(OH) ₄	15.41	94.67	Ref.S1
CuPd/TiO ₂	15	70	Ref.S2
Cu SA/NC	18	71	Ref.S3
Cu MPs	29	83.2	Ref.S4
CuO	10	70	Ref.S5
Cu plate	10	75	Ref.S6
Pd/C	5	62	Ref.S7
Cu NPs	40	80	Ref.S8

Table S3. Electrocatalytic semi-hydrogenation of C_2H_2 performance comparison between Cu/Ho₂O₃ and previously reported materials.

	•			0	, 2 3,	, 25	
Samples			CN	R (Å)	ΔE ₀	σ²	R factor
Cu/Ho ₂ O ₃	Cu	Cu-Cu	3.23	2.55	1.47	0.0096	0.0065
		Cu-O	2.22	1.94	1.47	0.0086	0.0050
	Но	Ho-O	2.47	2.28	0.45	0.0086	0.0064
Cu foil	Cu	Cu-Cu	3.64	2.54	4.94	0.0089	0.0028
bulk Ho ₂ O ₃	Но	Ho-O	4.15	2.26	2.71	0.0079	0.0031

Table S4. Structure parameters extracted from the EXAFS fitting of Cu/Ho₂O₃, Cu foil, bulk Ho₂O₃.

CN: coordination numbers; **R**: bond distance; σ^2 : Debye-Waller factors; ΔE_0 : the inner potential correction. **R factor**:

goodness of fit; the SO^2 was set to 1.0.

Reference

- 1 Z. Wang, C. Li, G. Peng, R. Shi, L. Shang, T. Zhang. Angew. Chem. Int. Ed. 2024, 63, e202400122.
- 2 M. R. Ball, K. R. Rivera-Dones, E. B. Gilcher, S. F. Ausman, C. W. Hullfish, E. A. Lebrón, J. A. Dumesic. ACS Catal. 2022, **10**, 8567-8581. Z. Jiang, L. Tang, L. Dong, X. Sheng, W. Zhang, Z. Liu, J. Shen, H. Jiang, C. Li. Angew. Chem. Int. Ed.
- 3 2023, **135**, e202307848.
- 4 S. Wang, K. Uwakwe, L. Yu, J. Ye, Y. Zhu, J. Hu, R. Chen, Z. Zhang, Z. Zhou, J. Li, Z. Xie, D. Deng. *Nat. Commun.* 2021, **12**, 7072.
- Z. Wu, J. Zhang, Q. Guan, X. Liu, H. Xiong, S. Chen, W. Hong, D. Li, Y. Lei, S. Deng, J. Wang, G. Wang. *Adv. Mater.* 2024, **36**, 2408681.
 T. Liu, J. Xiong, Q. Luo, S. Mao, Y. Wang. *ACS Catal.* 2024, **14**, 5838-5846.
 V. V. Chesnokov, O. Y. Podyacheva, R. M. Richards. *Mater. Res. Bull.* 2017, **88**, 78-84.

- X. Shi, Y. Lin, L. Huang, Z. Sun, Y. Yang, X. Zhou, E. Vovk, X. Liu, X. Huang, M. Sun, S. Wei, J. Lu. ACS Catal. 2020, **10**, 3495-3504.