Boosting alkaline hydrogen evolution performance of Co₄N porous

nanowires by interface engineering of CeO₂ tuning

Mengjie Lu,[‡]^a Duo Chen,[‡]^a Boran Wang,^c Ruiqing Li,^{*b} Dong Cai,^d Haoran Tu,^e Hang Yang,^a Yupu Zhang^a and Wei Han^{*a}

^a Sino-Russian International Joint Laboratory for Clean Energy and Energy Conversion Technology, College of Physics, International Center of Future Science, Jilin university, Changchun 130012, P.R. China. E-mail: <u>whan@jlu.edu.cn</u>

^b School of Chemistry and Chemical Engineering, Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, Liaocheng University, Liaocheng, 252059, China. E-mail: <u>liruiqing16@163.com</u>

^c State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China.

^d.Key Laboratory of Carbon Materials of Zhejiang Province, Wenzhou University, Wenzhou, 325035, P.R. China.

^e DongGuan University of Technology, DongGuan, 523808, P. R. China.

‡ These authors contributed equally to this work.



Figure S1. Optical pictures of as-prepared samples.



Figure S2. The enlarged XRD patterns of the CO₄N-CeO₂/NF.



Figure S3. Typical SEM images of the starting Ni foam.



Figure S4. SEM image of Co_3O_4 -CeO₂/NF nanowires on Ni foam.



Figure S5. The low-resolution SEM image of Co₄N-CeO₂/NF-2 nanoarrays

on Ni foam



Figure S6. HRTEM images of Co₄N-CeO₂/NF.



Figure S7. SEM image of pure Co_4N on Ni foam.



Figure S8. SEM images of pure CeO₂ on Ni foam.



Figure S9. Digtial images of air bubbles on (a) blank Ni foam and (b) Co_4N -

 $CeO_2/NF-2.$



Figure S10. HER polarization curves of Co_4N -CeO₂/NF-2 electrodes in different electrolyte of 0.1 M KOH, 30 wt% KOH and PBS buffer solution.



Figure S11. HER polarization curves of the Co_4N -CeO₂/NF-2 electrode compared to the physical mixture of Co_4N and CeO2 casted on the Ni foam.



Figure S12. Typical cyclic voltammograms at different scan rates. (a) $Co_4N-CeO_2/NF-1$, (b) $Co_4N-CeO_2/NF-2$, (c) $Co_4N-CeO_2/NF-3$, (d) Co_4N/NF and (e) CeO_2/NF with scan rates ranging from 10 mV/s to 100 mV/s.



Figure S13. Characterizations after the HER stability test. (a) The XRD pattern and (b) SEM image of Co_4N -CeO₂/NF-2 after HER stability test.



Figure S14. XPS spectra of (a) survey, (b) Co 2p, (C) N 1s, (d) Ce 3d, and (e)

O 1s for the Co_4N -CeO₂/NF-2 electrode after HER stability test.



Figure S15. The atomic percentage of N element before and after HER stability test.



Figure S16. Experimental and theoretical calculated amount of the evolved H_2 over the Co₄N-CeO₂/NF-2 electrode at a constant current density of 200 mA cm⁻² in 1.0 M KOH electrolyte.



Figure S17. The HER polarization curves without *iR*-correction of the Co_4N -CeO₂/NF-2 different sweep speeds.

Table S1. Comparison of the electrocatalytic HER activity for Co_4N -

Catalysts	Substrate	n _{j=10} (mV)	b (mV dec⁻¹)	Refs
Ni/CeO ₂	CNT	91		S1
CoN/Ni₃N	Carbon cloth	68	69	S2
Cu ₄ N/Ni ₃ N	Carbon cloth	71.4	106.5	S3
Mo_2N/Mo_2C	GC	152	68	S4
CoP/NiCoP	Ti foil	133	88	S5
Co ₃ O ₄ -CeO ₂	Carbon cloth	90	57.8	S6
NF@NiFe LDH/CeO _x	Ni foam	154	101	S7
Ni_3N -CeO $_2$	Ti mesh	80	122	S8
Co ₄ N-CeO ₂	Ni foam	52	56.8	This work

CeO₂/NF and reported catalysts in 1.0 M KOH electrolyte.

Table S2. Comparison of the electrocatalytic HER activity for Co_4N -CeO₂/NF and reported catalysts at high current density of 50 or 100 mA

Catalysts	Substrate	η _{j=50/100} (mV)	Refs
Ni_3S_2/MnO_2	Ni foam	η ₁₀₀ =197	S9
NiFe	Ni foam	η ₁₀₀ =142	S10
LDH@Ni₃N			
Ni _x Co ₃₋	Ni foam	η ₁₀₀ =258	S11
$_{x}S_{4}/Ni_{3}S_{2}$			
Co-doped	Cu foam	η ₁₀₀ =132	S12
CeO ₂			
CeO ₂ -Cu ₃ P	Ni foam	η ₅₀ =228	S13
NiFe	Ni foam	η ₁₀₀ =267	S14
LDH/CeO _x			
$Sn-Ni_3S_2$	Ni foam	η ₁₀₀ =171	S15
CoNi/CoFe ₂ O ₄	Ni foam	η ₁₀₀ =189	S16
Co_4N -CeO ₂	Ni foam	η ₁₀₀ =149	This
			work

cm⁻² in 1.0 M KOH electrolyte.

References

- [S1]. Z. Weng, W. Liu, L. C. Yin, R. Fang, M. Li, E. I. Altman, Q. Fan, F. Li, H. M. Cheng and H. Wang, Nano lett., 2015, 15, 7704-7710.
- [S2]. C. Ray, S. C. Lee, B. Jin, A. Kundu, J. H. Park and S. Chan Jun, J. Mater. Chem. A, 2018, 6, 4466-4476.
- [S3]. Z. Wang, L. Xu, F. Huang, L. Qu, J. Li, K. A. Owusu, Z. Liu, Z. Lin, B. Xiang, X. Liu, K. Zhao, X. Liao,
 W. Yang, Y. B. Cheng and L. Mai, *Adv. Energy Mater.*, 2019, **9**, 1900390.
- [S4]. Z. Lv, M. Tahir, X. Lang, G. Yuan, L. Pan, X. Zhang and J.-J. Zou, J. Mater. Chem. A, 2017, 5, 20932-20937.
- [S5]. Y. Lin, K. Sun, S. Liu, X. Chen, Y. Cheng, W. C. Cheong, Z. Chen, L. Zheng, J. Zhang, X. Li, Y. Pan and C. Chen, Adv. Energy Mater., 2019, 9, 1901213.
- [S6]. B. Liu, J. Cheng, H.-Q. Peng, D. Chen, X. Cui, D. Shen, K. Zhang, T. Jiao, M. Li, C.-S. Lee and W. Zhang, J. Mater. Chem. A, 2019, 7, 775-782.
- [S7]. X. Wang, Y. Yang, L. Diao, Y. Tang, F. He, E. Liu, C. He, C. Shi, J. Li, J. Sha, S. Ji, P. Zhang, L. Ma and N. Zhao, ACS Appl. Mater. Interfaces, 2018, 10, 35145-35153.
- [S8]. Z. Sun, J. Zhang, J. Xie, X. Zheng, M. Wang, X. Li and B. Tang, *Inorg. Chem. Front.*, 2018, 5, 3042-3045.
- [S9]. Y. Xiong, L. L. Xu, C. D. Jin and Q. F. Sun, Appl. Catal., B, 2019, 254, 329–338.
- [S10]. B. R. Wang, S. H. Jiao, Z. S. Wang, M. J. Lu, D. Chen, Y. T. Kang, G. S. Pang and S. H. Feng, J. Mater. Chem. A, 2020, 8, 17202-17211.
- [S11]. Y. Wu, Y. Liu, G.-D. Li, X. Zou, X. Lian, D. Wang, L. Sun, T. Asefa and X. Zou, Nano Energy, 2017, 35, 161–170.
- [S12]. S. Jiang, R. Zhang, H. Liu, Y. Rao, Y. Yu, S. Chen, Q. Yue, Y. Zhang and Y. Kang, J. Am. Chem. Soc., 2020, 142, 6461-6466.
- [S13]. Z. Wang, H. Du, Z. Liu, H. Wang, A. M. Asiri and X. Sun, Nanoscale, 2018, 10, 2213-2217.
- [14]. X. Wang, Y. Yang, L. Diao, Y. Tang, F. He, E. Liu, C. He, C. Shi, J. Li, J. Sha, S. Ji, P. Zhang, L. Ma and N. Zhao, ACS Appl. Mater. Interfaces, 2018, 10, 35145-35153.
- [S15]. J. Jian, L. Yuan, H. Qi, X. Sun, L. Zhang, H. Li, H. Yuan and S. Feng, ACS Appl. Mater. Interfaces, 2018, 10, 40568–40576.
- [S16]. S. S. Li, S. Sirisomboonchai, A. Yoshida, X. W. An, X. G. Hao, A. Abudula and G. Q. Guan, J. Mater. Chem. A, 2018, 6, 19221–19230.