

Supporting information

Interface-engineered urchin-like CoFe-layered double hydroxide for high-efficiency electrocatalytic oxygen evolution

Xuxu Sun,^{a,b,‡} Ruiqi Wang,^{a,b,‡} Qi Wang,^{a,b,c,*} Kostya (Ken) Ostrikov^d

^a *Institute of Plasma Physics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031 Anhui, China*

^b *University of Science and Technology of China, Hefei 230026 Anhui, China*

^c *College of Chemical Engineering, Sichuan University of Science and Engineering, Zigong 643000, China*

^d *School of Chemistry and Physics and QUT Centre for Materials Science, Queensland University of Technology (QUT), Brisbane, QLD 4000, Australia*

[‡] These authors contributed equally to this work;

Corresponding Author: Qi Wang, E-mail: qiwang@ipp.ac.cn;

Results

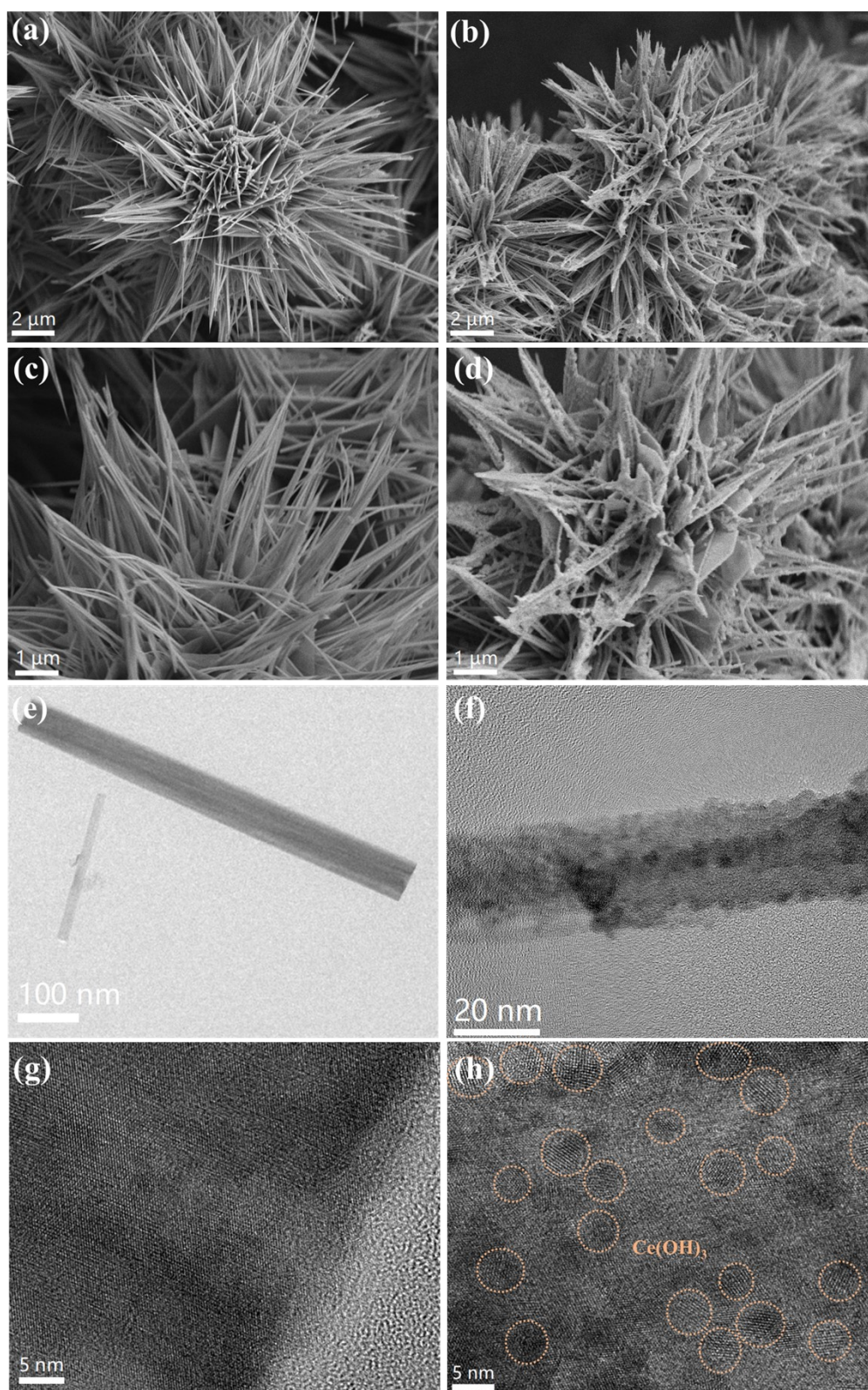


Figure S1. SEM images of (a, c) CoFe-LDH, and (b, d) Ce@CoFe-LDH; TEM images of (e) CoFe-LDH and (f) Ce@CoFe-LDH; HRTEM images of (g) CoFe-LDH and (h) Ce@CoFe-LDH.

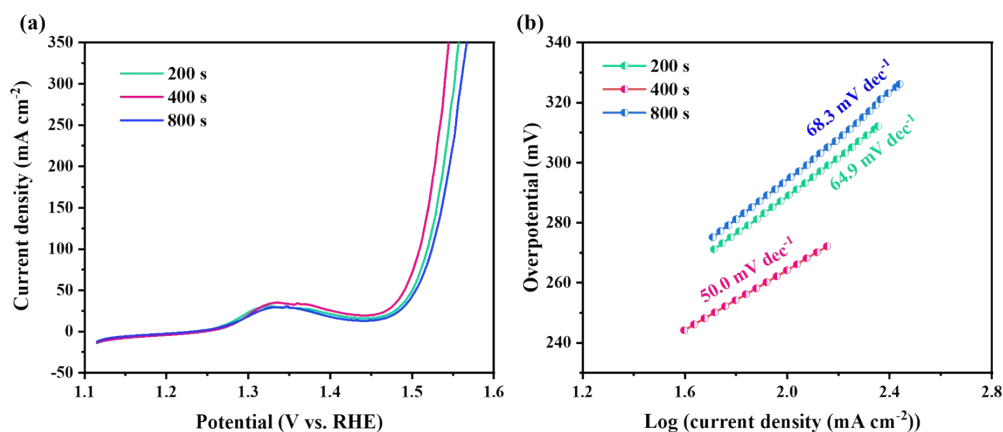


Figure S2. (a) LSV curves and (b) Tafel plots corresponding to different electrodeposition time for Ce@CoFe-LDH samples.

Table S1. Comparative OER performance of our Ce@CoFe-LDH with state-of-the-art OER electrocatalysts

Samples	Electrolyte	Overpotential (mV)	Tafel slop (mV/d ec)	Ref.
Ce@CoFe-LDH	1 M KOH	207	50	This work
NiFe-LDH@NiCoP/NF	1 M KOH	220	48.6	[1]
Co ₉ S ₈ @NiFe-LDH	1 M KOH	220	52	[2]
PA-ZnCoFe-LDH	1 M KOH	221	58.7	[3]
NiFe-LDHs-V _{Ni}	1 M KOH	229	62.9	[4]
FeCo-LDH@Co(OH) ₂ -0.5	1 M KOH	230	75.8	[5]
Mn-NiFe-LDH/rGO	1 M KOH	240	40	[6]
CoFeV-LDH/NF	1 M KOH	242	57	[7]
S-FeOOH/IF	1 M KOH	244	59	[8]
NiFeCo-LDH/CF	1 M KOH	249	42	[9]

CoFe@NC/CC	1 M KOH	254	54.9	[10]
Ni ₃ S ₄ @CoFe-LDH	1 M KOH	262	70.2	[11]
Fe-Co ₉ S ₈ @SNC	1 M KOH	273	55.8	[12]
(Co,Ni)Se ₂ @NiFe-LDH	1 M KOH	277	75	[13]

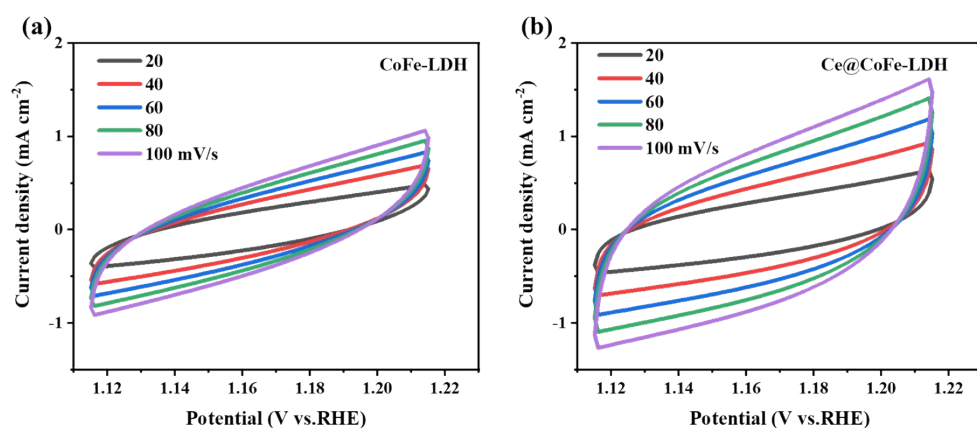


Figure S3. CV curves of (a) CoFe-LDH and (b) Ce@CoFe-LDH samples at different scan rates from 20 to 100 mV s⁻¹ for the calculation of C_{dl} .

Table S2. Performance comparison of Ce@CoFe-LDH and CoFe-LDH catalysts.

Samples	Catalytic activity				
	Overpotential (mV)	Tafel slop (mV dec ⁻¹)	Specific	TOF (s ⁻¹)	R _{ct} (ohm)
			activity (mA		
			cm ⁻²)		
@ 300 mV overpotential					
Ce@CoFe-LDH	207	50.0	2.23	0.0512	3.15
CoFe-LDH	232	74.2	1.20	0.0121	4.5

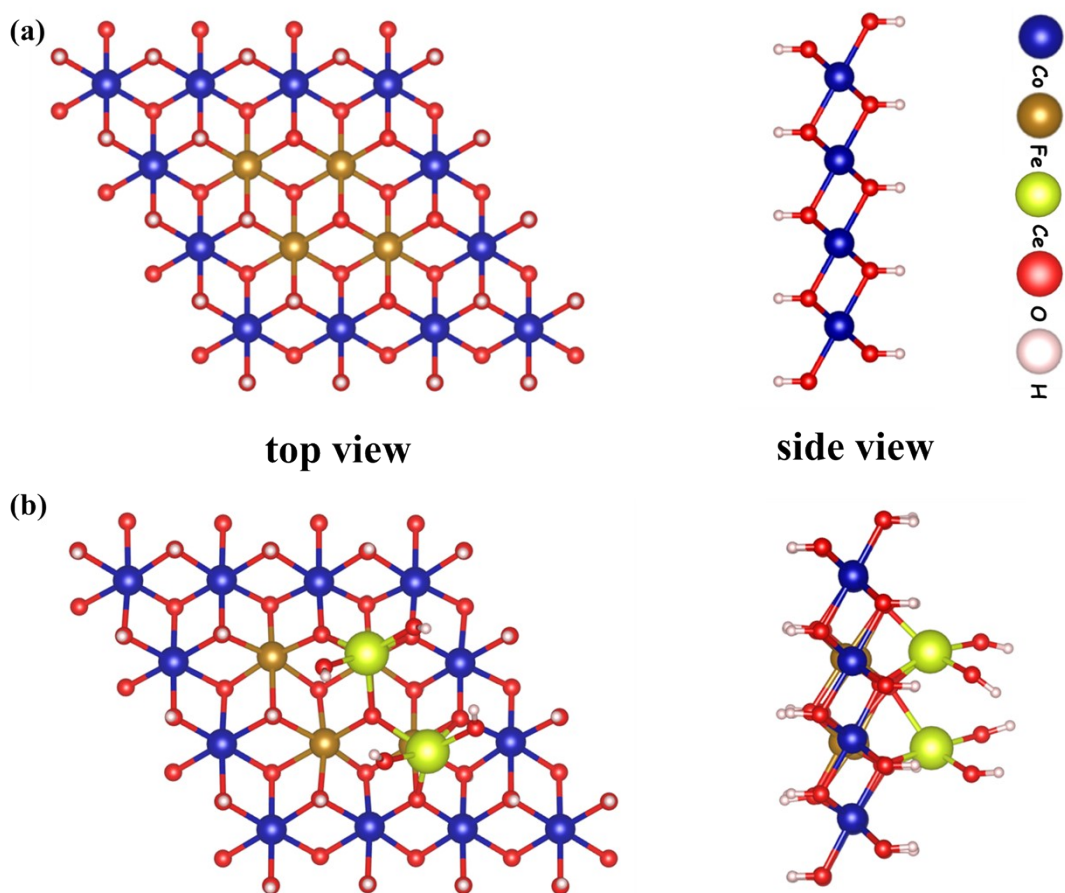


Figure S4. Structural models of (a) CoFe-LDH and (b) Ce@CoFe-LDH catalysts.

Table S3. Calculated Gibbs free energy values of Ce@CoFe-LDH and CoFe-LDH catalysts.

Samples	Gibbs free energy values (eV)			
	$\text{H}_2\text{O} \rightarrow * \text{OH}$	$* \text{OH} \rightarrow * \text{O}$	$* \text{O} \rightarrow * \text{OOH}$	$* \text{OOH} \rightarrow \text{O}_2$
Ce@CoFe-LDH	-0.14	0.25	-0.04	-0.07
CoFe-LDH	0.29	0.56	-0.47	-0.38

Table S4. Comparative performance of our Ce@CoFe-LDH with state-of-the-art electrocatalysts for overall water splitting.

Samples	Electrolyte	Cell voltage (V) @10 mA cm ⁻²	Ref.
Ce@CoFe-LDH	1 M KOH	1.47	This work

CoFe-250	1 M KOH	1.47	[14]
Ni ₃ S ₂ -FeS-CoS/PNFCF	1 M KOH	1.48	[15]
NiTe-NeSe/NFF	1 M KOH	1.49	[16]
S-FeOOH/IF	1 M KOH	1.50	[8]
MoS ₂ -AB (75)	1 M KOH	1.51	[17]
Cr-Fe ₃ O ₄ -N/NF	1 M KOH	1.53	[18]
Ti ₃ C ₂ @mNiCoP	1 M KOH	1.57	[19]
NiFe-LDH@NiCoP	1 M KOH	1.57	[1]
S-NiFeOOH	1 M KOH	1.57	[20]
CoFe@NiFe-200/NF	1 M KOH	1.59	[21]
CoP@NCFs	1 M KOH	1.59	[22]
NiCo ₂ S ₄ @NiFe-LDH	1 M KOH	1.60	[23]
Ni-SA@NCA	1 M KOH	1.66	[24]

References

- 1 H. Zhang, X. Li, A. Hähnel, V. Naumann, C. Lin, S. Azimi, S.L. Schweizer, A.W. Maijenburg, R.B. Wehrspohn, Bifunctional heterostructure assembly of NiFe LDH nanosheets on NiCoP nanowires for highly efficient and stable overall water splitting, *Advanced Functional Materials*, 2018, **28**, 1706847.
- 2 X. Feng, Q. Jiao, Z. Dai, Y. Dang, S.L. Suib, J. Zhang, Y. Zhao, H. Li, C. Feng, A. Li, Revealing the effect of interfacial electron transfer in heterostructured Co₉S₈@NiFe LDH for enhanced electrocatalytic oxygen evolution, *Journal of Materials Chemistry A*, 2021, **9**, 12244-12254.
- 3 J. Han, J. Zhang, T. Wang, Q. Xiong, W. Wang, L. Cao, B. Dong, Zn doped FeCo layered double hydroxide nanoneedle arrays with partial amorphous phase for efficient oxygen evolution reaction, *ACS Sustainable Chemistry & Engineering*, 2019, **7**, 13105-13114.

- 4 Y. Wang, M. Qiao, Y. Li, S. Wang, Tuning surface electronic configuration of NiFe LDHs nanosheets by introducing cation vacancies (Fe or Ni) as highly efficient electrocatalysts for oxygen evolution reaction, *Small*, 2018, **14**, 1800136.
- 5 X. Yang, J. Cheng, Y. Xu, H. Li, W. Tu, J. Zhou, Heterogeneous ultra-thin FeCo-LDH@Co(OH)₂ nanosheets facilitated electrons transfer for oxygen evolution reaction, *Chemical Engineering Journal*, 2023, **472**, 145076.
- 6 B. Jiang, W. C. Cheong, R. Tu, K. Sun, S. Liu, K. Wu, H. Shang, A. Huang, M. Wang, L. Zheng, X. Wei, C. Chen, Regulating the electronic structure of NiFe layered double hydroxide/reduced graphene oxide by Mn incorporation for high-efficiency oxygen evolution reaction, *Science China Materials*, 2021, **64**, 2729-2738.
- 7 Y. Hu, Z. Wang, W. Liu, L. Xu, M. Guan, Y. Huang, Y. Zhao, J. Bao, H. M. Li, Novel cobalt–iron–vanadium layered double hydroxide nanosheet arrays for superior water oxidation performance, *ACS Sustainable Chemistry & Engineering*, 2019, **7**, 16828-16834.
- 8 X. Chen, Q. Wang, Y. Cheng, H. Xing, J. Li, X. Zhu, L. Ma, Y. Li, D. Liu, S-doping triggers redox reactivities of both iron and lattice oxygen in FeOOH for low-cost and high-performance water oxidation, *Advanced Functional Materials*, 2022, **32**, 2112674.
- 9 Y. Lin, H. Wang, C. K. Peng, L. Bu, C. L. Chiang, K. Tian, Y. Zhao, J. Zhao, Y. G. Lin, J. M. Lee, L. Gao, Co-induced electronic optimization of hierarchical NiFe LDH for oxygen evolution, *Small*, 2020, **16**, 2002426.
- 10 Q. Liu, X. Liu, Y. Xie, F. Sun, Z. Liang, L. Wang, H. Fu, N-doped carbon coating enhances the bifunctional oxygen reaction activity of CoFe nanoparticles for a highly stable Zn–air battery, *Journal of Materials Chemistry A*, 2020, **8**, 21189-21198.
- 11 A. Karmakar, D. Mahendiran, R. Madhu, P. Murugan, S. Kundu, Bypassing the scaling relationship with spin selectivity: Construction of lewis base-functionalized heterostructural 2D nanosheets for enhanced oxygen evolution reaction, *Journal of Materials Chemistry A*, 2023, **11**, 16349-16362.
- 12 W. Wang, Y. Yang, Y. Zhao, S. Wang, X. Ai, J. Fang, Y. Liu, Multi-scale regulation in S, N co-incorporated carbon encapsulated Fe-doped Co₉S₈ achieving efficient water oxidation with low overpotential, *Nano Research*, 2021, **15**, 872-880.
- 13 J. G. Li, H. Sun, L. Lv, Z. Li, X. Ao, C. Xu, Y. Li, C. Wang, Metal–organic framework-derived hierarchical (Co,Ni)Se₂@NiFe LDH hollow nanocages for enhanced oxygen evolution, *ACS Applied Materials & Interfaces*, 2019, **11**, 8106-8114.
- 14 Q. Zhang, M. Sun, J. Zhu, S. Yang, L. Chen, X. Yang, P. Wang, K. Li, F. Xue, Y. Lu, J. Zhang, P. Zhao, New strategy to synthesize oxygen vacancy-rich CoFe nanoneedles for overall water splitting and urea electrolysis, *Chemical Engineering Journal*, 2022, **432**, 134275.
- 15 Q. Zhang, W. Chen, G. Chen, J. Huang, C. Song, S. Chu, R. Zhang, G. Wang, C. Li, K. K. Ostrikov, Bi-metallic nitroxide nanodot-decorated tri-metallic sulphide nanosheets by on-electrode plasma-hydrothermal sprouting for overall water splitting, *Applied Catalysis B: Environmental*, 2020, **261**, 118254.
- 16 J. Wang, J. Huang, G. Chen, W. Chen, T. Li, A. Meng, K. Ostrikov, In-situ engineered heterostructured nickel telluride nanosheets for robust overall water splitting, *Chemical Engineering Journal*, 2022, **446**, 137297.
- 17 L. Guo, Q. Liu, Y. Liu, Z. Chen, Y. Jiang, H. Jin, T. Zhou, J. Yang, Y. Liu, Self-supported tremella-like MoS₂-AB particles on nickel foam as bifunctional electrocatalysts for overall water splitting, *Nano Energy*, 2022, **92**, 106707.
- 18 S. Meng, S. Sun, Y. Liu, Y. Lu, M. Chen, Synergistic modulation of inverse spinel Fe₃O₄ by doping with chromium and nitrogen for efficient electrocatalytic water splitting, *Journal of Colloid and Interface Science*, 2022, **624**, 433-442.
- 19 Q. Yue, J. Sun, S. Chen, Y. Zhou, H. Li, Y. Chen, R. Zhang, G. Wei, Y. Kang, Hierarchical mesoporous Mxene–NiCoP electrocatalyst for water-splitting, *ACS Applied Materials & Interfaces*, 2020, **12**, 18570-18577.
- 20 C. Kim, S.H. Kim, S. Lee, I. Kwon, S.H. Kim, S. Kim, C. Seok, Y.S. Park, Y. Kim, Boosting overall water splitting by incorporating sulfur into NiFe (oxy)hydroxide, *Journal of Energy Chemistry*, 2022, **64**, 364-371.
- 21 R. Yang, Y. Zhou, Y. Xing, D. Li, D. Jiang, M. Chen, W. Shi, S. Yuan, Synergistic coupling of CoFe-LDH arrays with NiFe-LDH nanosheet for highly efficient overall water splitting in alkaline media, *Applied Catalysis B: Environmental*, 2019, **253**, 131-139.

- 22 L. Zhi, J. Tu, J. Li, M. Li, J. Liu, 3D holey hierarchical nanoflowers assembled by cobalt phosphide embedded N-doped carbon nanosheets as bifunctional electrocatalyst for highly efficient overall water splitting, *Journal of Colloid and Interface Science*, 2022, **616**, 379-388.
- 23 J. Liu, J. Wang, B. Zhang, Y. Ruan, L. Lv, X. Ji, K. Xu, L. Miao, J. Jiang, Hierarchical $\text{NiCo}_2\text{S}_4@\text{NiFe}$ LDH heterostructures supported on nickel foam for enhanced overall-water-splitting activity, *ACS Applied Materials & Interfaces*, 2017, **9**, 15364-15372.
- 24 Y. Cheng, H. Guo, X. Li, X. Wu, X. Xu, L. Zheng, R. Song, Rational design of ultrahigh loading metal single-atoms (Co, Ni, Mo) anchored on in-situ pre-crosslinked guar gum derived N-doped carbon aerogel for efficient overall water splitting, *Chemical Engineering Journal*, 2021, **410**, 128359.