

In-situ Generated α -Co(OH)₂/Co₃Mo derived from Co-Mo-N for enhanced electrochemical hydrogen evolution reaction

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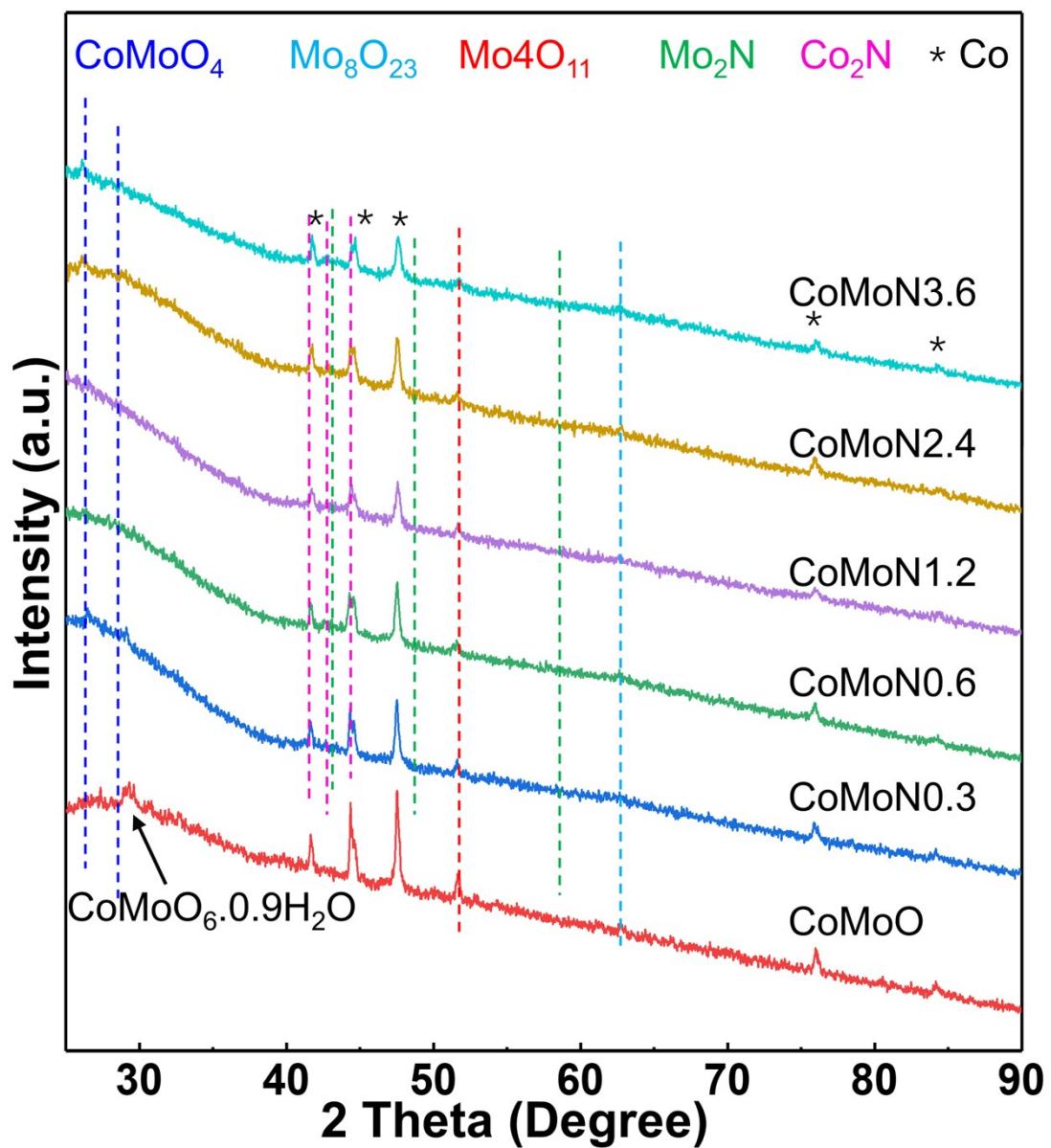


Figure S1. XRD of the CoMoO precursor and samples treated under different N

content.

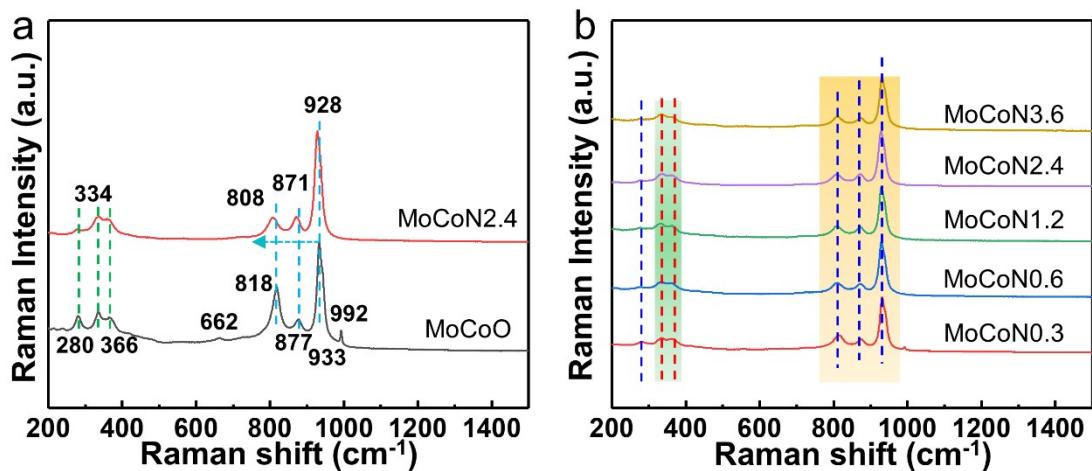


Figure S2. Raman spectra of the CoMoO precursor and CoMoN with different N

content.

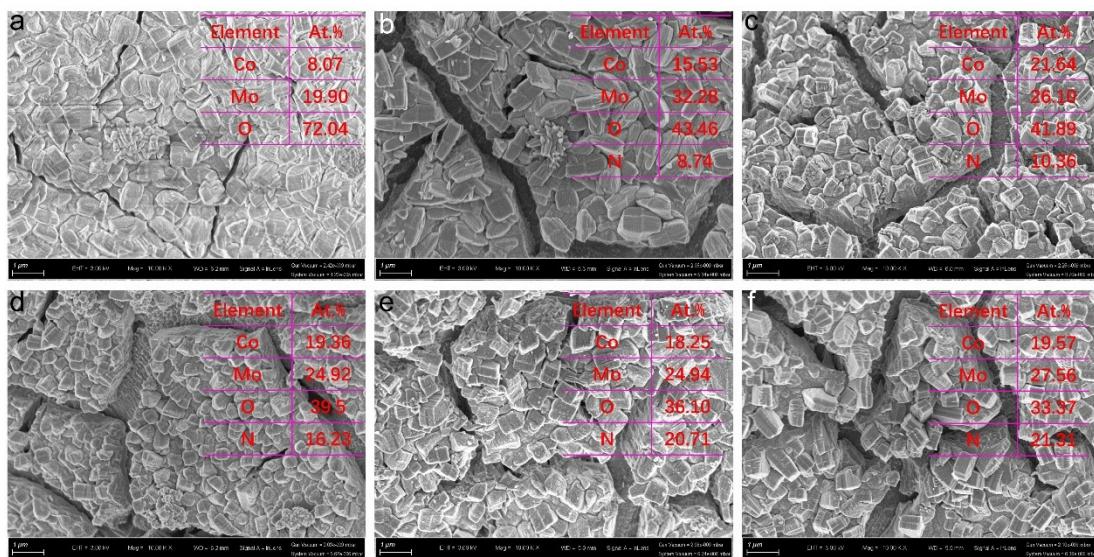


Figure S3. SEM and EDS of the catalysts. (a) CoMoO precursor, (b) CoMoN0.3,

(c) CoMoN0.6, (d) CoMoN1.2, (e) CoMoN2.4, (f) CoMoN3.6.

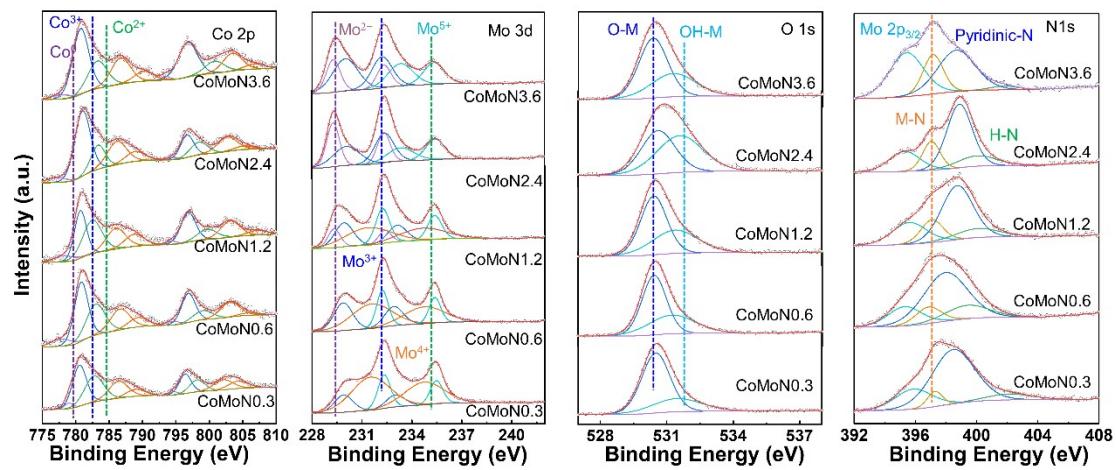


Figure S4. High-resolution XPS spectra of Co 2p, Mo 3d, O 1s, and N 1s in CoMoN with different N content.

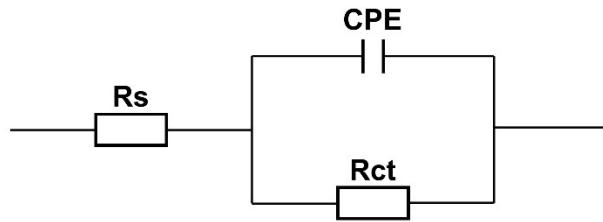


Figure S5. The equivalent circuit for the samples.

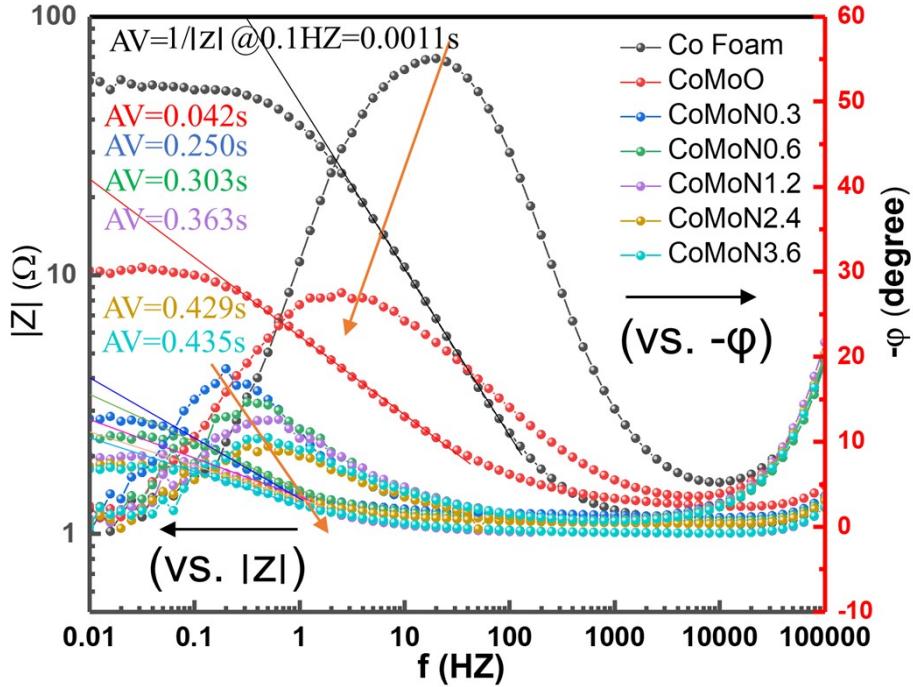


Figure S6. The Bode plots of the samples according to Figure 3c.

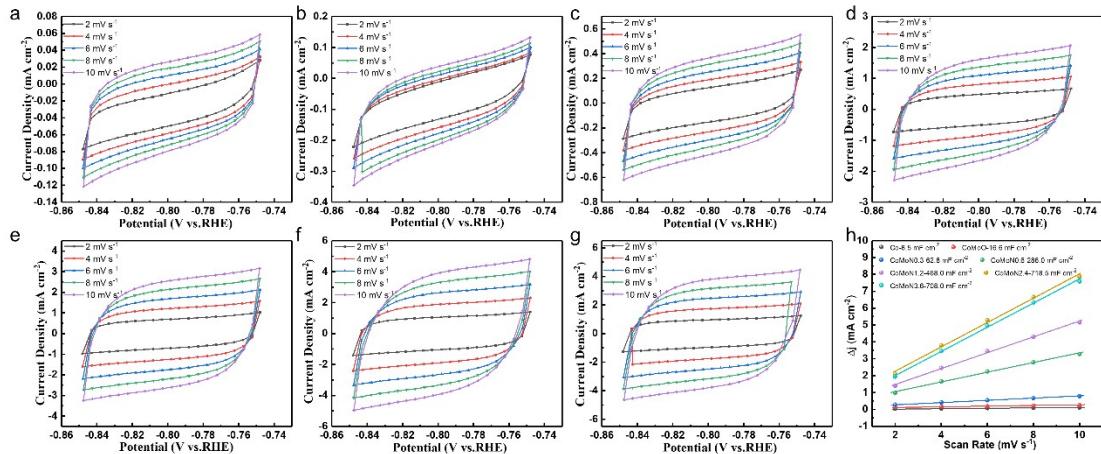


Figure S7. CV curves under different scan rates of Co foam (a), CoMoO (b), CoMoN (0.3), CoMoN (0.6), CoMoN (1.2), CoMoN (2.4), and CoMoN (3.6), and the corresponding C_{dl} calculated from the CV curves.

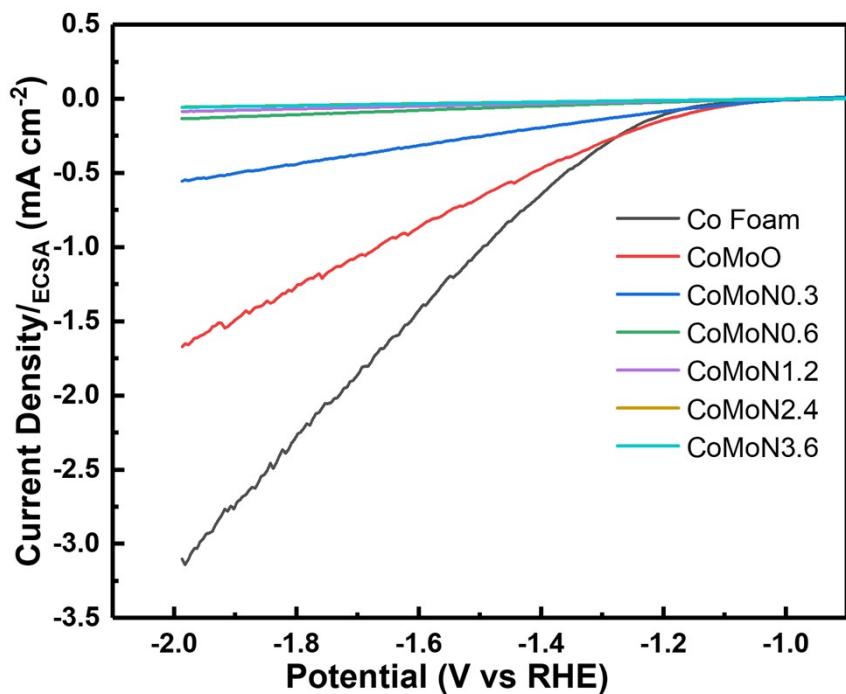


Figure S8 ECSA normalized LSV curves of the samples for HER, $\text{ECSA} = \text{C}_{\text{dl}}/\text{C}_s (\text{C}_s = 0.04 \text{ mF cm}^{-2})^1$, the Current Density/ ECSA = the current density/ECSA.

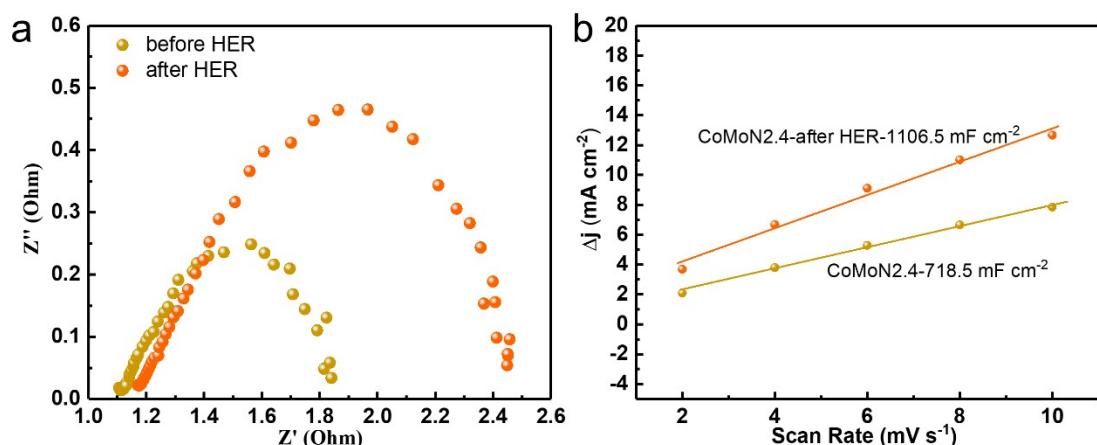


Figure S9. The electrochemical impedance spectroscopies (EIS) and electrochemical double-layer capacitance (C_{dl}) of the CoMoN2.4 before and after the HER long-term stability test.

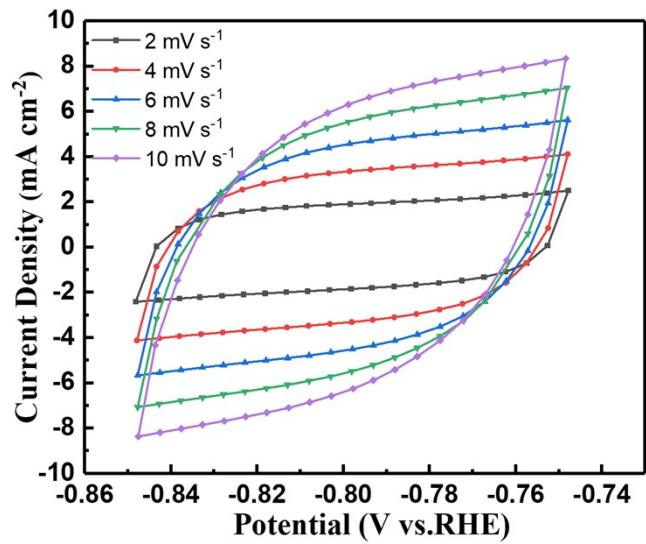


Figure S10. CV curves under different scan rates of CoMoN2.4 after HER stability

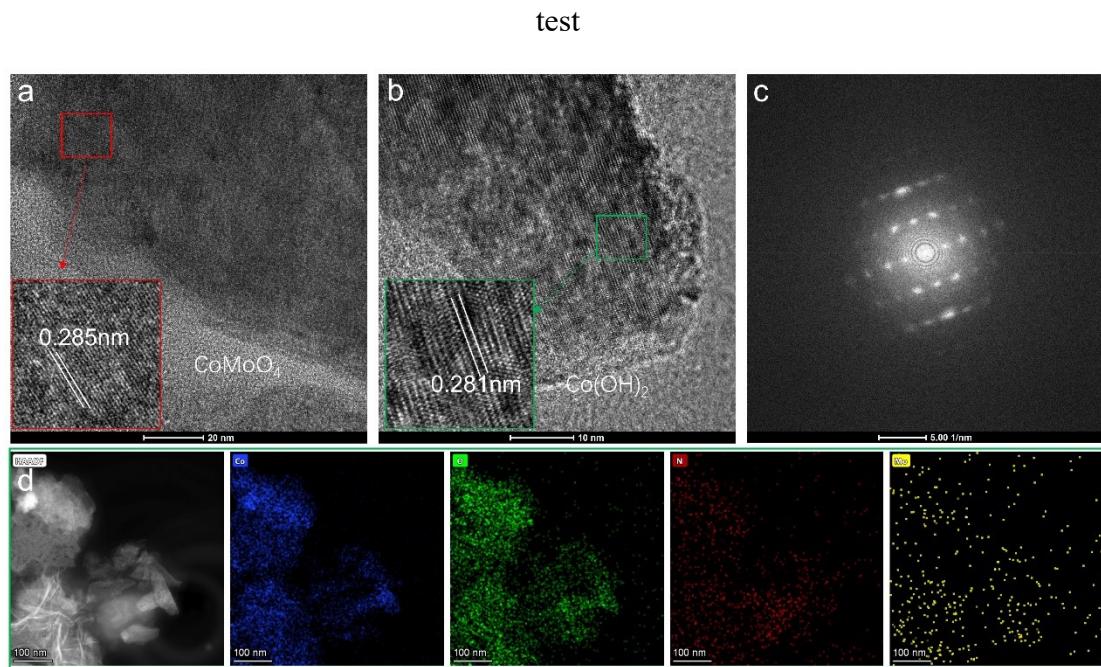


Figure S11. HRTEM images (a) and (b), corresponding SAED pattern of b (c), and EDS mappings (d) of CoMoN2.4.

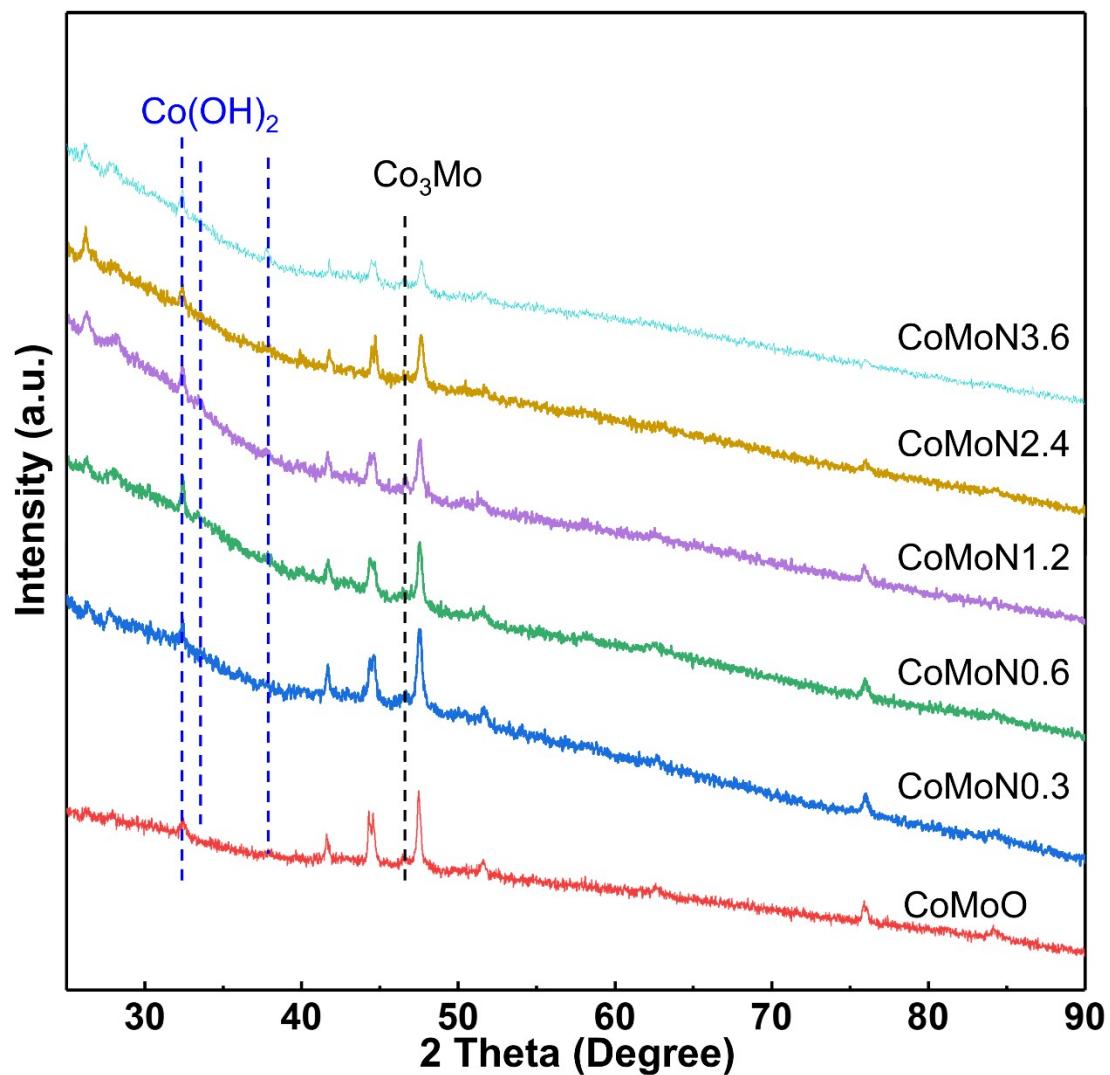


Figure S12. XRD pattern of the samples after a short-time HER test.

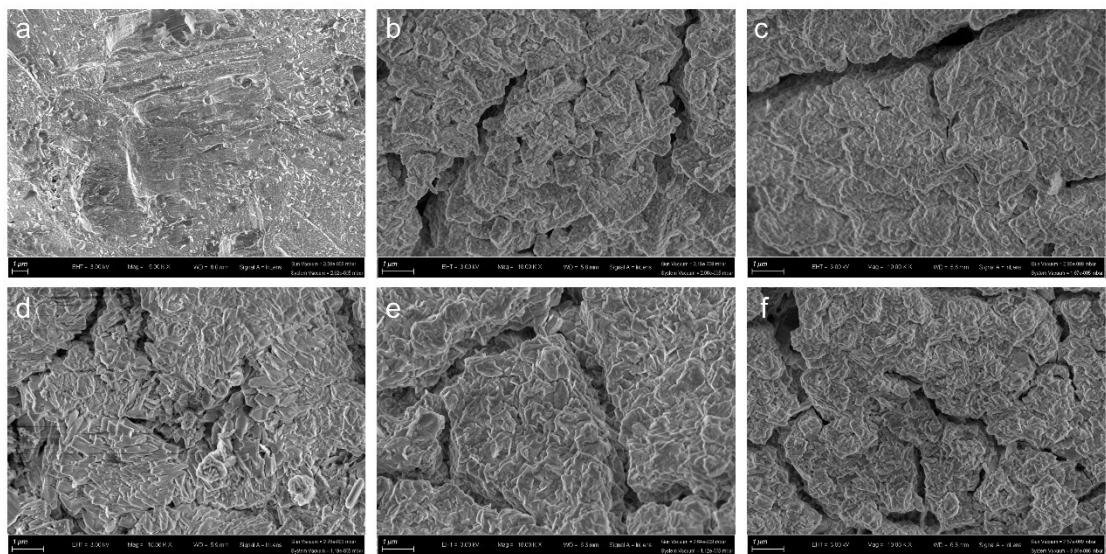


Figure S13. SEM of the catalysts after a short-time HER test. (a) CoMoO precursor, (b) CoMoN0.3, (c) CoMoN0.6, (d) CoMoN1.2, (e) CoMoN2.4, (f) CoMoN3.6.

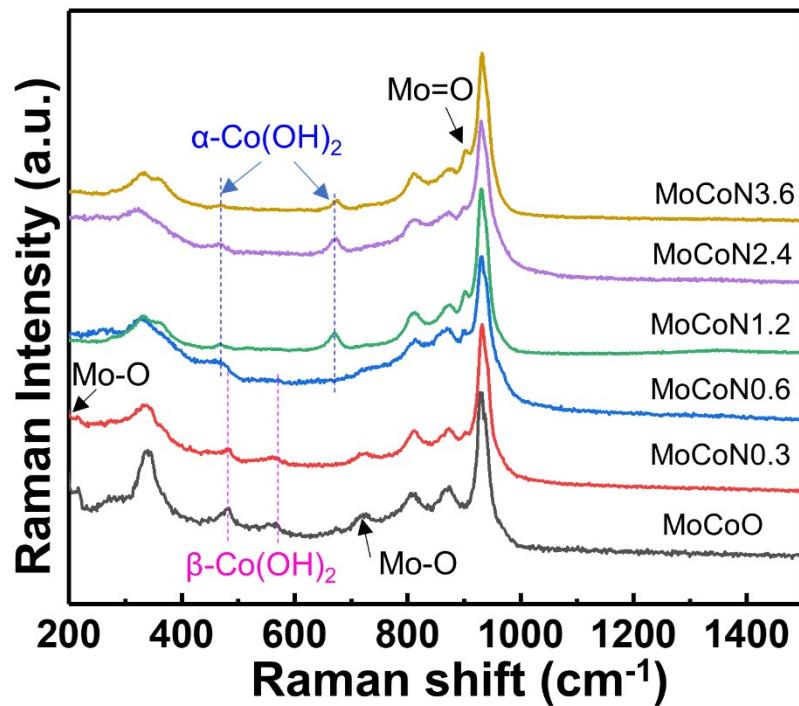


Figure S14. Raman spectra of the samples after a short-time HER test.

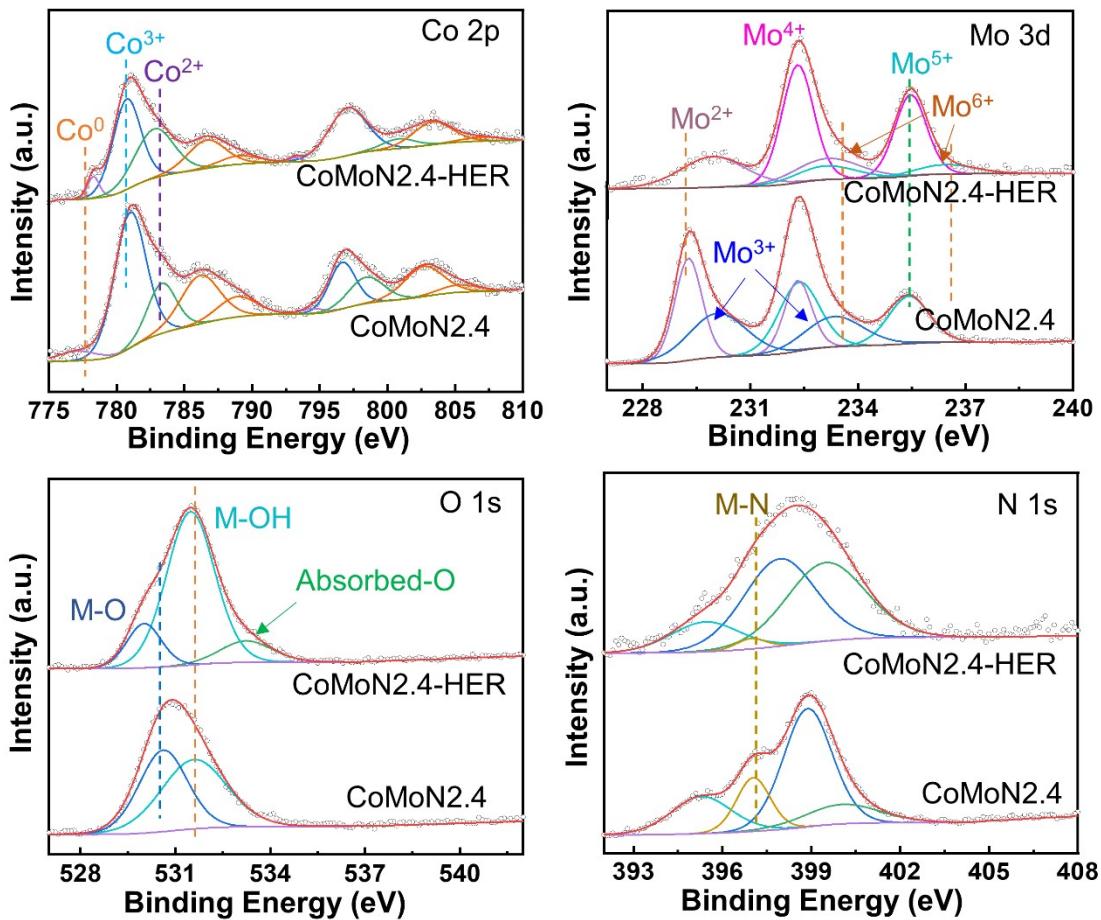


Figure S15. High-resolution XPS spectra of Co 2p, Mo 3d, O 1s, and N 1s in CoMoN2.4 before and after HER long-term stability.

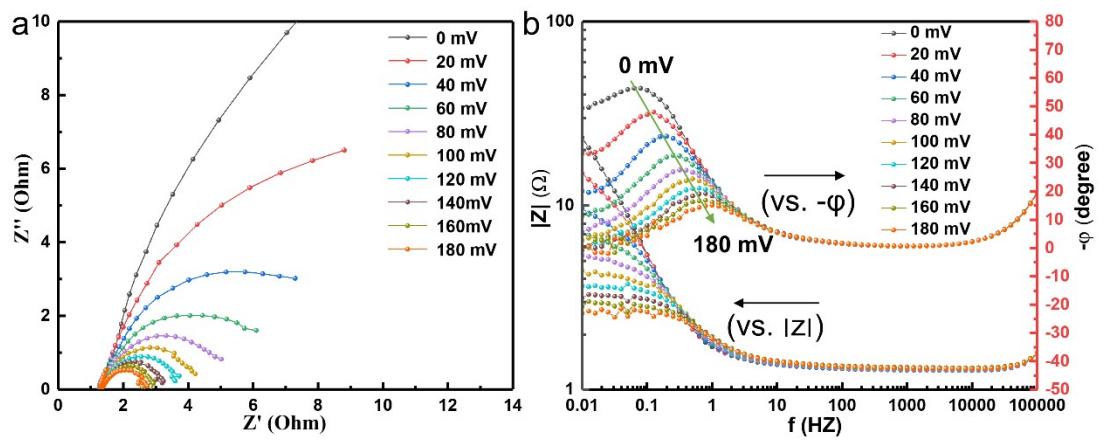


Figure S16. The Nyquist (a) and Bode frequency-resistance plots (b) of CoMoN2.4 under different overpotentials.

Table S1. The HER performance comparison of the nitrides in 1 M KOH.

Note: NF, CC, CFC, CP, and CF represent Ni Foam, Carbon Cloth, Carbon Fiber Cloth, Carbon Paper, and Co Foam, respectively. Y and NA represent Yes and Not Available.

Samples	Preparation Methods	Overpotential under a certain current density	Stability under a certain current density	IR correction	References
$\text{Ni}_3\text{N}_{1-x}/\text{NF}$	N_2 plasma	55 mV, 10 mA cm ⁻²	50h, 50 mA cm ⁻²	NA	2
$\text{Ni}_3\text{N}/\text{NF}$	Electrodeposition+	12 mV, 10 mA cm ⁻²	50h, 10 mA cm ⁻²	Y	3
	Nitridation in NH_3				
$\text{P,Ce-FeNi}_3\text{N}/\text{NF}$	Hydrothermal	153 mV, 100 mA cm ⁻² 21.3 mV, 10 mA cm ⁻²	50h, 50 mA cm ⁻²	Y	4
$\text{Ni}_2\text{Mo}_3\text{N}/\text{NF}$	Annealed	89 mV, 50 mA cm ⁻² 123.8 mV, 100 mA cm ⁻²	24h, 10 mA cm ⁻²	Y	5
$\text{Ni}_3\text{N}/\text{NF}$	Oxided+Nitridation in NH_3	171.9 mV, 50 mA cm ⁻² 207.3 mV, 100 mA cm ⁻²	20h, 24 mA cm ⁻²	Y	6

Cr-Co ₄ N/CC	Hydrothermal+	21 mV, 10 mA cm ⁻²	150h, 10 mA cm ⁻²	NA	7
	Nitridation in urea	99 mV, 100 mA cm ⁻²			
CoN/CC	Hydrothermal+	150mV, 10 mA cm ⁻²	---	NA	7
	Nitridation in urea	330 mV, 100 mA cm ⁻²			
NiMoN/NF	Hydrothermal+	56mV, 100 mA cm ⁻²	48h, 100/500 mA cm ⁻²	Y	8
	Nitridation in NH ₃	127 mV, 500 mA cm ⁻²			
VN _x N/CP	Hydrothermal+	95 mV, 10 mA cm ⁻²	12h, 10 mA cm ⁻²	NA	9
	Nitridation in NH ₃				
Co-Ni ₃ N/NFF	Hydrothermal+	194 mV, 10 mA cm ⁻²	24h, 10-50 mA cm ⁻²	NA	10
	Nitridation in NH ₃				
Cu ₁ Ni ₂ -N/CFC	Solvothermal+	71.4 mV, 10 mA cm ⁻²	60h, 10 mA cm ⁻²	NA	11
	Nitridation in NH ₃				
W ₂ N ₃ -powder	Nitridation in NH ₃	379 mV, 10 mA cm ⁻²	---	NA	12
cRu-Ni ₃ N/NF	Hydrothermal+	32 mV, 10 mA cm ⁻²	100h, 50 mA cm ⁻²	Y	13
	Nitridation in NH ₃	99 mV, 100mA cm ⁻²			

Ni ₃ N/NF	Hydrothermal+	92 mV, 10 mA cm ⁻²	---	Y	13
	Nitridation in NH ₃	125 mV, 100mA cm ⁻²			
Co-Mo ₅ N ₆ /NFF	Hydrothermal+	19 mV, 10 mA cm ⁻²	10h, 10/50/1000 mA cm ⁻²	Y	14
	Nitridation in NH ₃	280 mV, 1000 mA cm ⁻²			
NiMoN/CC	Electrodeposition+N ₂ plasma	109 mV, 10 mA cm ⁻²	12h, 10/30/50 mA cm ⁻²	NA	15
	Hydrothermal+N ₂ plasma	150 mV, 10 mA cm ⁻²			
CoMoN _{0.3} /CF	Hydrothermal+	74mV, 10 mA cm ⁻²	---	NA	This work
	Nitridation in urea	231mV, 100 mA cm ⁻²			
CoMoN _{0.6} /CF	Hydrothermal+	678mV, 500 mA cm ⁻²	---	NA	This work
	Nitridation in urea	51mV, 10 mA cm ⁻²			
CoMoN _{1.2} /CF	Hydrothermal+	194mV, 100 mA cm ⁻²	---	NA	This work
		616mV, 500 mA cm ⁻²			
		42mV, 10 mA cm ⁻²	---	NA	This work

	Nitridation in urea	180mV, 100 mA cm ⁻²			
CoMoN _{2.4} /CF	Hydrothermal+	595mV, 500 mA cm ⁻²			
		37mV, 10 mA cm ⁻²			
	Nitridation in urea	164mV, 100 mA cm ⁻²	110h, 10-600 mA cm ⁻²	NA	This work
CoMoN _{3.6} /CF	Hydrothermal+	578mV, 500 mA cm ⁻²			
		35mV, 10 mA cm ⁻²			
	Nitridation in urea	164mV, 100 mA cm ⁻²	---	NA	This work
		585mV, 500 mA cm ⁻²			

References:

- 1.P. Zhou; P. Niu; J. Liu; N. Zhang; H. Bai; M. Chen; J. Feng; D. Liu; L. Wang; S. Chen; C. T. Kwok; Y. Tang; R. Li; S. Wang; H. Pan, *Adv. Funct. Mater.*, 2022, **32**, 2202068.
2. Bin Liu; Bin He; Hui-Qing Peng; Yufei Zhao; unye Cheng; Jing Xia; Jianhua Shen; Tsz-Wai Ng; Xiangmin Meng; Chun-Sing Lee; W. Zhang, *Adv. Sci. (Weinh)*, 2018, **5**, 1800406.
3. Fuzhan Song; Wei Li; Jiaqi Yang; Guanqun Han; Peilin Liao; Y. Sun., *Nat. Commun.*, 2018, **9**, 4531.
4. Shuangshuang Li; Yunmei Du; Mengmeng Wang; Jie Liu; Bin Li; Yuanxiang Gu; L. Wang., *Sci. China Mater.*, 2023, **66**, 4639-4649.
5. Sang Heon Park; a. M. H. L. Tae Hwan Jo; Kenta Kawashima; C. Buddie Mullins; Hyung-Kyu Lim; D. H. Youn., *J. Mater. Chem. A*, 2021, **9**, 4945.
6. Chikaodili E. Chukwuneke; Kenta Kawashima; Hao Li; Raul A. Marquez; Yoon Jun Son; Lettie A. Smith; Hugo Celio; Graeme Henkelman; C. B. Mullins., *J. Mater. Chem. A*, 2024, **12**, 1654.
7. N. Yao; P. Li; Z. Zhou; Y. Zhao; G. Cheng; S. Chen; W. Luo, *Adv. Energy Mater.*, 2019, **9**, 1902449.
8. L. Yu; Q. Zhu; S. Song; B. McElhenny; D. Wang; C. Wu; Z. Qin; J. Bao; Y. Yu; S. Chen; Z. Ren, *Nat. Commun.*, 2019, **10**, 5106.
9. R. Tong; Z. Sun; F. Zhang; X. Wang; J. Xu; X. Shi; S. Wang; H. Pan, *ACS Sustainable Chem. Eng.*, 2018, **6**, 16525-16531.
10. C. Zhu; A. L. Wang; W. Xiao; D. Chao; X. Zhang; N. H. Tiep; S. Chen; J. Kang; X. Wang; J. Ding; J. Wang; H. Zhang; H. J. Fan, *Adv. Mater.*, 2018, **30**, e1705516.
11. Zhaoyang Wang; Lin Xu; Fuzhi Huang; Longbing Qu; Jiantao Li; Kwadwo Asare Owusu; Ziang Liu; Zifeng Lin; Binhua Xiang; Xiong Liu; Kangning Zhao; Xiaobin Liao; Wei Yang; Yi-Bing Cheng; L. Mai, *Adv. Energy Mater.*, 2019, **9**, 1900390.
12. R. Tong; Y. Qu; Q. Zhu; X. Wang; Y. Lu; S. Wang; H. Pan, *ACS Appl. Energy Mater.*, 2019, **3**, 1082-1088.
13. J. Zhu; R. Lu; W. Shi; L. Gong; D. Chen; P. Wang; L. Chen; J. Wu; S. Mu; Y. Zhao, *Energy Environ. Mater.*, 2023, **6**, e12318.

14. F. Lin; Z. Dong; Y. Yao; L. Yang; F. Fang; L. Jiao, *Adv. Energy Mater.*, 2020, **10**, 2002176.
15. Y. Zhang; B. Ouyang; J. Xu; S. Chen; R. S. Rawat; H. J. Fan, *Adv. Energy Mater.*, 2016, **6**, 1600221.
16. Xi Wang; Fengyu Qiao; Chao Sun; Jipeng Zhu; Bo Ouyang; E. Kan., *J. Electron. Mater.*, 2023, **52**, 1740-1748.