

Supporting Information

Highly active and durable NiMoCuCo catalyst with moderated hydroxide adsorption energy for efficient hydrogen evolution reaction in alkaline media

Hyeonggeun Choi^{a,1}, Seunghwan Jo^{a,1}, Ki Hoon Shin^a, HeeYoung Lim^b, Liting Zhang^a, Keon Beom Lee^a, Young-Woo Lee^{b,c,}, Jung Inn Sohn^{a,*}*

^a Division of Physics and Semiconductor Science, Dongguk University-Seoul, Seoul 04620 Republic of Korea

^b Department of Energy Engineering, Soonchunhyang University, Asan 31538, Republic of Korea

^c Advanced Energy Research Center, Soonchunhyang University, Asan 31538, Republic of Korea

¹ These authors contributed equally to this work.

*Corresponding author.

E-mail address: ywlee@sch.ac.kr (Y.-W. Lee), junginn.sohn@dongguk.edu (J.I. Sohn).

Keywords: ternary transition metal, water electrolysis, hydrogen evolution reaction, water dissociation, metal dissolution

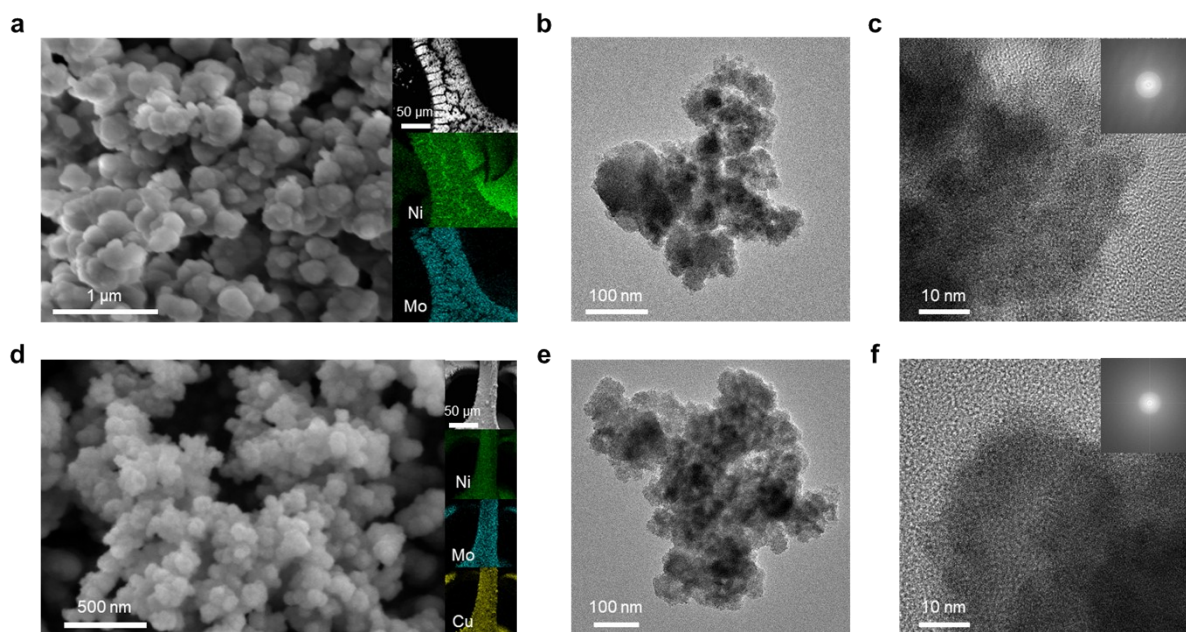


Fig. S1 (a) FE-SEM (left) and EDS (right) images of NiMo. (b) FE-TEM and (c) high-resolution TEM images of NiMo. The inset shows a fast Fourier transform image. (d) FE-SEM (left) and EDS (right) images of NiMoCu. (e) FE-TEM and (f) high-resolution TEM images of NiMoCu. The inset shows a fast Fourier transform image.

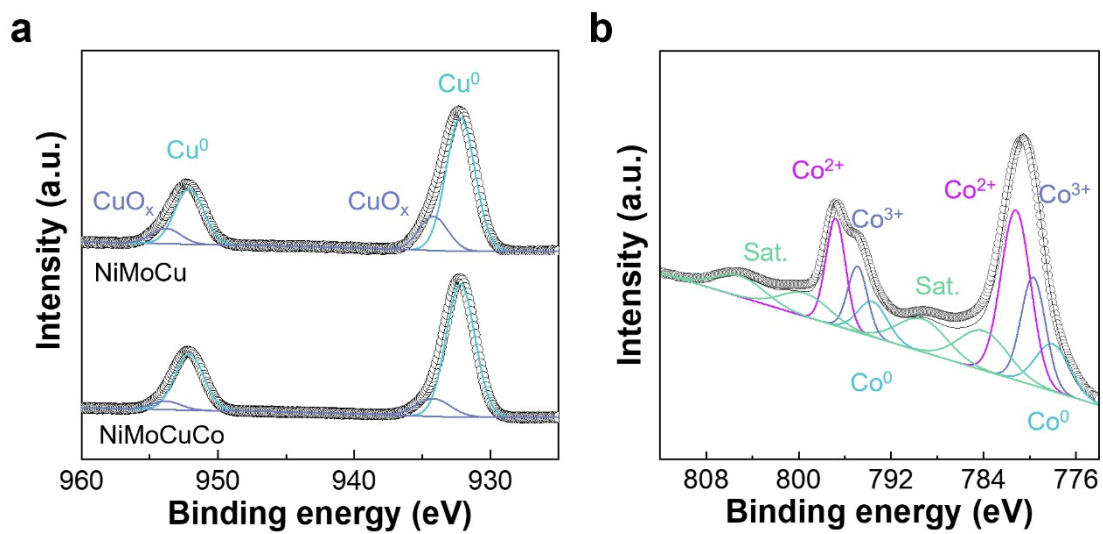


Fig. S2 XPS spectra of the prepared electrocatalysts in (a) Cu 2*p* and (b) Co 2*p* regions.

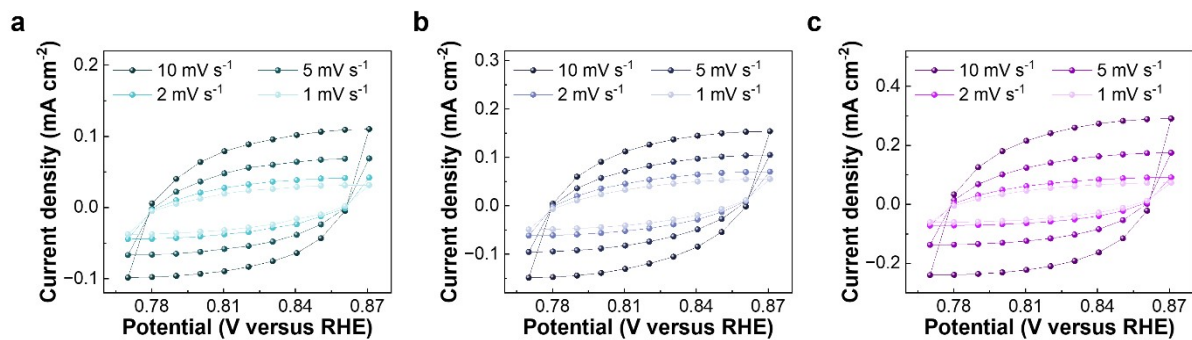


Fig. S3 Cyclic voltammety curves of (a) NiMo, (b) NiMoCu, and (c) NiMoCuCo.

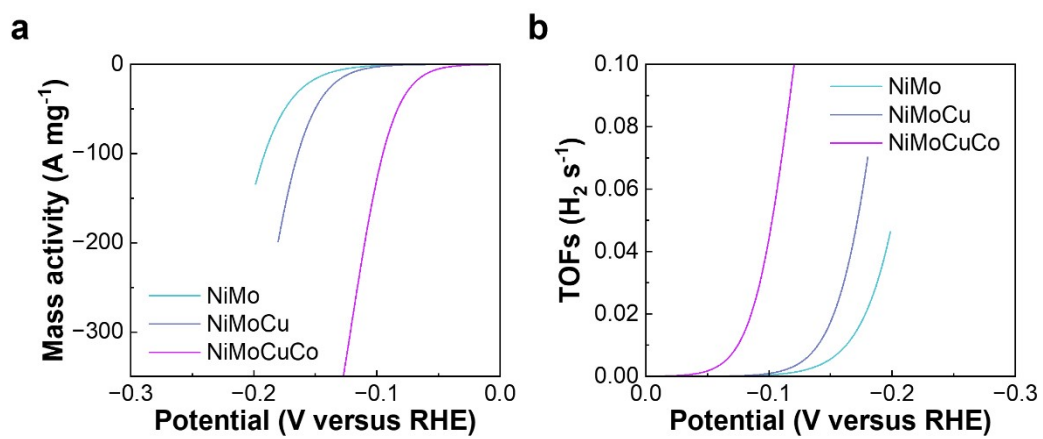


Fig. S4 Polarization curves normalized by (a) loading mass and (b) turnover frequency.

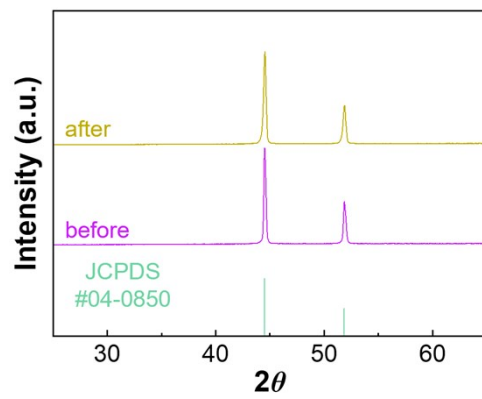


Fig. S5 XRD patterns of NiMoCuCo before and after the long-term stability test.

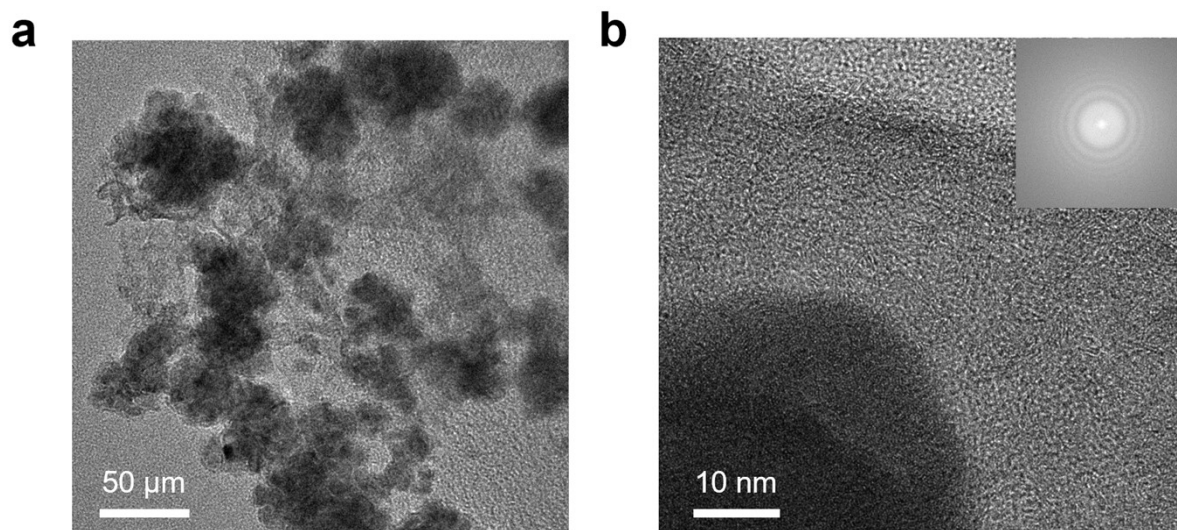


Fig. S6 (a) FE-TEM and (b) high-resolution TEM images of NiMoCuCo after the long-term stability test. The inset shows a fast Fourier transform image.

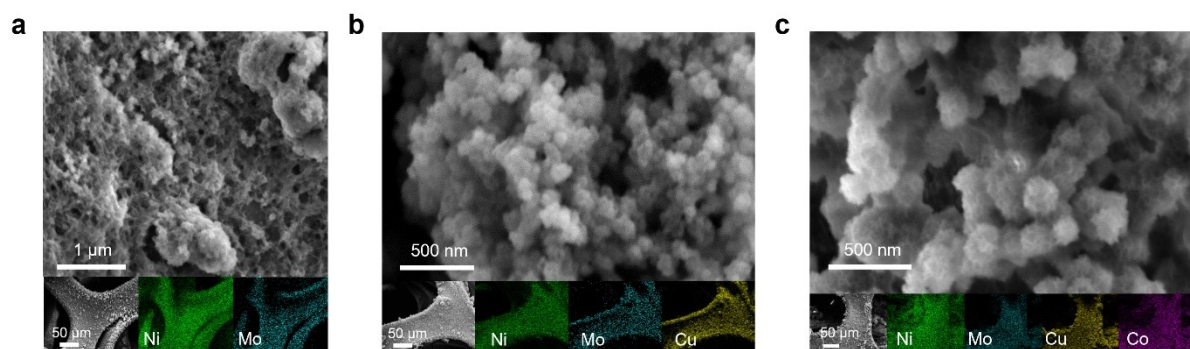


Fig. S7 FE-SEM (top) and EDS (bottom) images of (a) NiMo, (b) NiMoCu, and (c) NiMoCuCo.

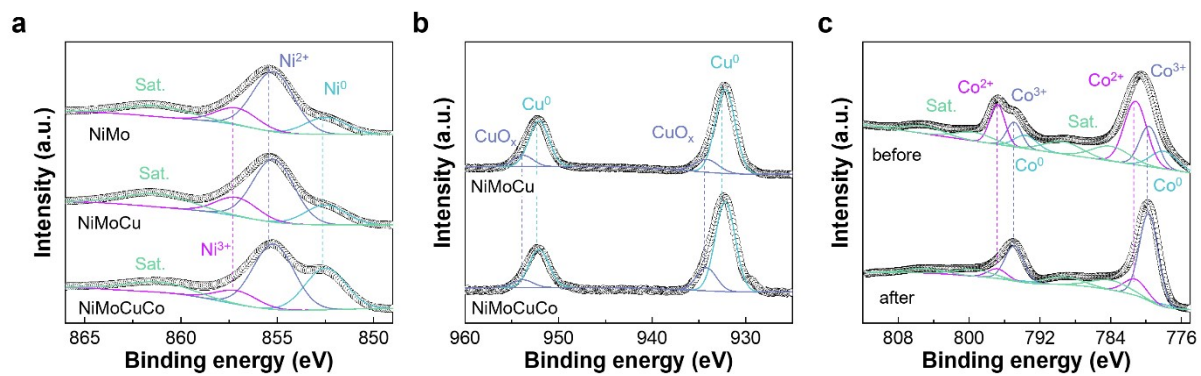


Fig. S8 XPS spectra of the long-term stability tested electrocatalysts in (a) Ni 2*p*, (b) Cu 2*p*, and (c) Co 2*p* regions.

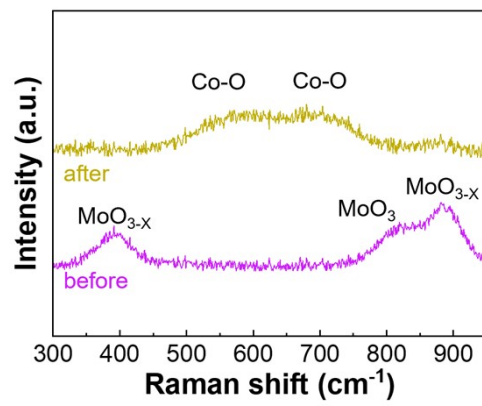


Fig. S9 Raman spectra of NiMoCuCo before and after the long-term stability test.

Table S1 Comparative analysis of the recently studied alkaline HER electrocatalysts with respect to the catalytic performance at a current density of 10 mA cm⁻².

Catalysts	Electrode	Overpotential (mV)	Tafel slope (mV dec ⁻¹)	Stability Condition	Stability time (h)	Ref.
NiMoCuCo	Ni foam	53	34.2	100 mA cm ⁻²	100	This work
VNMS	Graphite rod	122	57	-0.17 V versus RHE	10	1
Pt/NiRu-LDH	Ni foam	38	39	-0.075 V versus RHE	30	2
Se-MoS ₂ /CoSe ₂	Ni foam	30	44	100 mA cm ⁻²	40	3
RhSe ₂	Glassy carbon	81.6	96	10,000 cycle	-	4
O-NiCu	Iron foam	23	34.1	10 mA cm ⁻²	100	5
FeCoNiCuPd	Carbon cloth	29.7	47.2	100 mA cm ⁻²	36	6
Mo-NiS/Ni ₃ S ₂ -0.08S	Ni foam	73	115.7	1,000 cycle	-	7
MoS ₂ -MoP/NC	Carbon cloth	35	30	10,000 cycle	-	8
6B-Fe ₇ S ₈ /FeS ₂ /CC	Carbon cloth	113	57.4	1,000 cycle	-	9
NiP ₂ -650 (c/m)	Carbon cloth	134	67	50 mA cm ⁻²	14	10
CeO ₂ /CoS ₂ /Ti	Ti plate	36	38	40 mA cm ⁻²	1,000	11
1%Pt-NiCoP@Mxene	Carbon cloth	26.5	38.6	500 mA cm ⁻²	3,000	12
RRu-Ru ₂ P	Glassy carbon	95	31.99	1,000 mA cm ⁻²	1,000	13
NiVB@rGO	Glassy	196	88	Not	12	14

	carbon			mentioned		
Ni ₂ Cr ₁ -LDH	Nickel foam	138	61.5	-0.07 V versus RHE	30	15

Reference

- [1] S. Bolar, S. Shit, N.C. Murmu, P. Samanta, T. Kuila, Activation strategy of MoS₂ as HER electrocatalyst through doping-induced lattice strain, band gap engineering, and active crystal plane design, *ACS Appl. Mater. Interfaces*, 2021, **13**, 1, 765-780
- [2] D. Li, X. Chen, Y. Lv, G. Zhang, Y. Huang, W. Liu, Y. Li, R. Chen, C. Nuckolls, H. Ni, An effective hybrid electrocatalyst for the alkaline HER: Highly dispersed Pt sites immobilized by a functionalized NiRu-hydroxide, *Appl. Catal. B*, 2020, **269**, 118824
- [3] L. Liao, J. Sun, D. Li, F. Yu, Y. Zhu, Y. Yang, J. Wang, W. Zhou, D. Tang, S. Chen, H. Zhou, Highly robust non-noble alkaline hydrogen-evolving electrocatalyst from Se-doped molybdenum disulfide particles on interwoven CoSe₂ nanowire arrays, *Small*, 2020, **16**, 1906629
- [4] W. Zhong, B. Xiao, Z. Lin, Z. Wang, L. Huang, S. Shen, Q. Zhang, L. Gu, RhSe₂: A superior 3D electrocatalyst with multiple active facets for hydrogen evolution reaction in both acid and alkaline solutions, *Adv. Mater.*, 2021, **33**, 2007894
- [5] J. Wang, S. Xin, Y. Xiao, Z. Zhang, Z. Li, W. Zhang, C. Li, R. Bao, J. Peng, J. Yi, S. Chou, Manipulating the water dissociation electrocatalytic sites of bimetallic nickel-based alloys for highly efficient alkaline hydrogen evolution, *Angew. Chem. Int. Ed.*, 2022, **61**, e202202518
- [6] S. Wang, B. Xu, W. Huo, H. Feng, X. Zhou, F. Fang, Z. Xie, J.K. Shang, J. Jiang, Efficient FeCoNiCuPd thin-film electrocatalyst for alkaline oxygen and hydrogen evolution reactions, *Appl. Catal. B*, 2022, **313**, 121472

- [7] K. Zhang, Y. Duan, N. Graham, W. Yu, Unveiling the synergy of polymorph heterointerface and sulfur vacancy in NiS/Ni₃S₂ electrocatalyst to promote alkaline hydrogen evolution reaction, *Appl. Catal. B*, 2023, **323**, 122144
- [8] X. Huang, H. Xu, D. Cao, D. Cheng, Interface construction of P-substituted MoS₂ as efficient and robust electrocatalyst for alkaline hydrogen evolution reaction, *Nano Energy*, 2020, **78**, 105253
- [9] J. Wu, Q. Zhang, K. Shen, R. Zhao, W. Zhong, C. Yang, H. Xiang, X. Li, N. Yang, Modulating interband energy separation of boron-doped Fe₇S₈/FeS₂ electrocatalysts to boost alkaline hydrogen evolution reaction, *Adv. Funct. Mater.*, 2022, **32**, 2107802
- [10] Q. Fu, X. Wang, J. Han, J. Zhong, T. Zhang, T. Yao, C. Xu, T. Gao, S. Xi, C. Liang, L. Xu, P. Xu, B. Song, Phase-junction electrocatalysts towards enhanced hydrogen evolution reaction in alkaline media, *Angew. Chem. Int. Ed.*, 2021, **133**, 263-271
- [11] J. Li, Z. Xia, Q. Xue, M. Zhang, S. Zhang, H. Xiao, Y. Ma, Y. Qu, Insights into the interfacial Lewis acid-base pairs in CeO₂-loaded CoS₂ electrocatalysts for alkaline hydrogen evolution, *Small*, 2021, **17**, 2103018
- [12] H.-J. Niu, C. Huang, T. Sun, Z. Fang, X. Ke, R. Zhang, N. Ran, J. Wu, J. Liu, W. Zhou, Enhancing Ni/Co activity by neighboring Pt atoms in NiCoP/MXene electrocatalyst for alkaline hydrogen evolution, *Angew. Chem. Int. Ed.*, 2024, **63**, e202401819
- [13] Q. Yu, W. Yu, Y. Wang, J. He, Y. Chen, H. Yuan, R. Liu, J. Wang, S. Liu, J. Yu, H. Liu, W. Zhou, Hydroxyapatite-derived heterogeneous Ru-Ru₂P electrocatalyst and environmentally-friendly membrane electrode toward efficient alkaline electrolyzer, *Small*, 2023, **19**, 2208045

[14] M. Arif, G. Yasin, M. Shakeel, M.A. Mushtaq, W. Ye, X. Fang, S. Ji, D. Yan, Highly active sites of NiVB nanoparticles dispersed onto graphene nanosheets towards efficient and pH-universal overall water splitting, *J. Energy Chem.*, 2021, **58**, 237-246

[15] W. Ye, X. Fang, X. Chen, D. Yan, A three-dimensional nickel-chromium layered double hydroxide micro/nanosheet array as an efficient and stable bifunctional electrocatalyst for overall water splitting, *Nanoscale*, 2018, **10**, 19484