Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2019

Supplementary Materials

Mo-Doped NiCu as an Efficient and Stable Electrocatalyst for Hydrogen Evolution Reaction

Zhengnan Wang, Xingbo Ge*, Zhihao Li, Jing Wu, Zihao Liang, Shuang Wang

School of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu, Sichuan 610500, PR China

** Corresponding author at: School of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu, Sichuan 610500, PR China*

E-mail addresses: xbge@swpu.edu.cn (X. Ge).

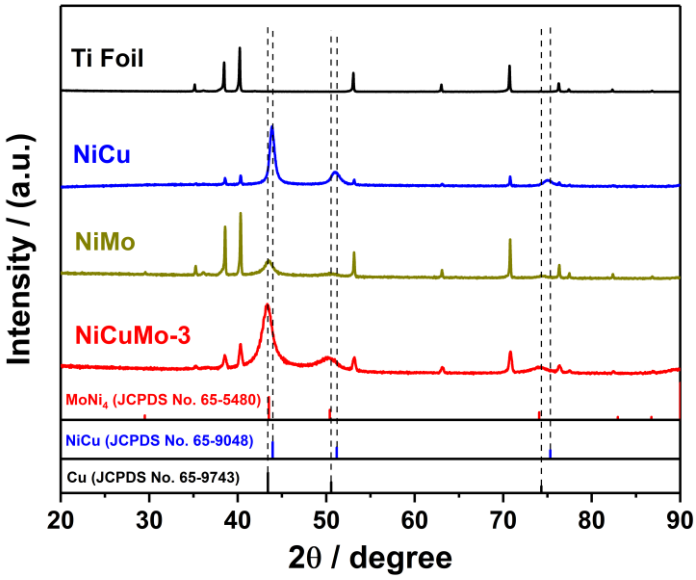

Fig. S1 XRD pattern of the as-prepared NiCuMo-3 (red), NiMo (green), and NiCu (blue) catalysts on Ti foil (black) and the corresponding standard pattern (red, blue, and black profile).

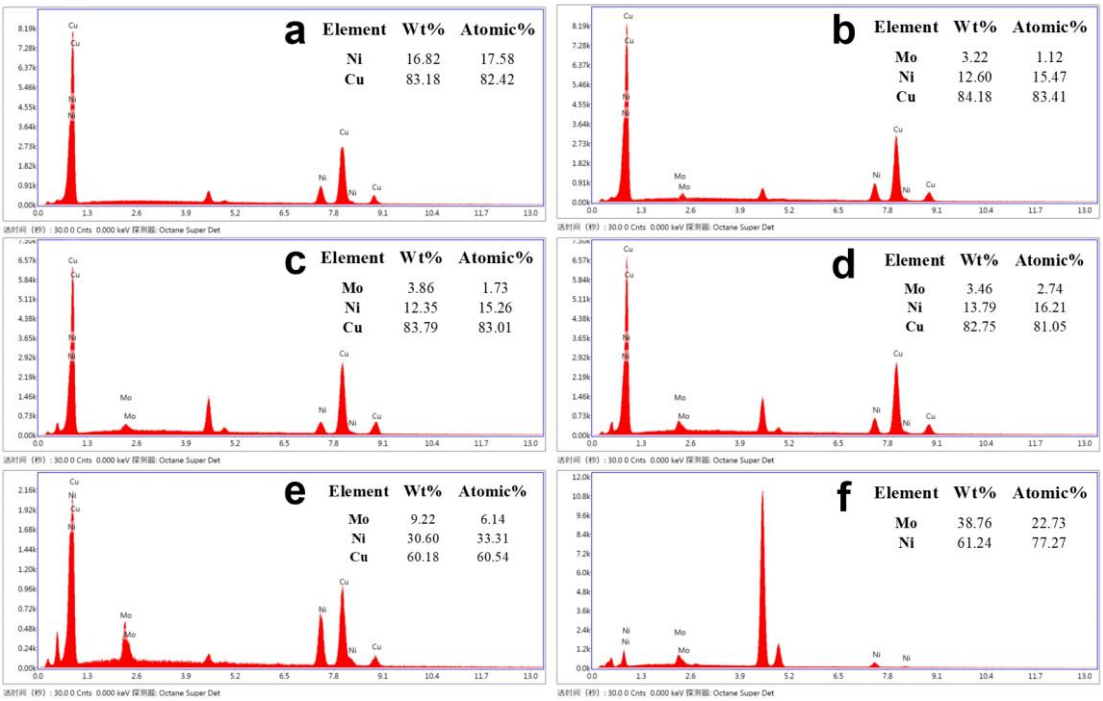

Fig. S2 EDS of as-prepared (a) NiCu, (b) NiCuMo-1 (1.1 at. % Mo), (c) NiCuMo-2 (1.7 at. % Mo), (d) NiCuMo-3 (2.7 at. % Mo), (e) NiCuMo-4 (6.1 at. % Mo) and (f) NiMo catalysts on Ti foil.

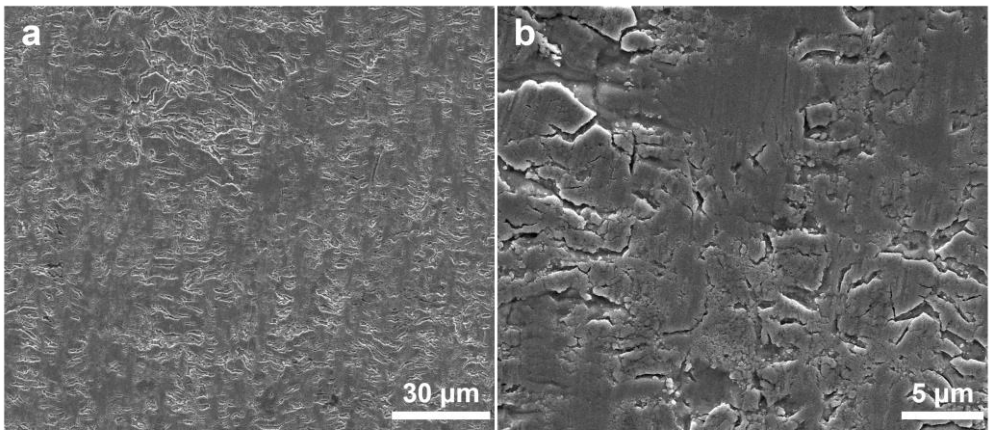

Fig. S3 SEM images of as-treated blank Ti foil.

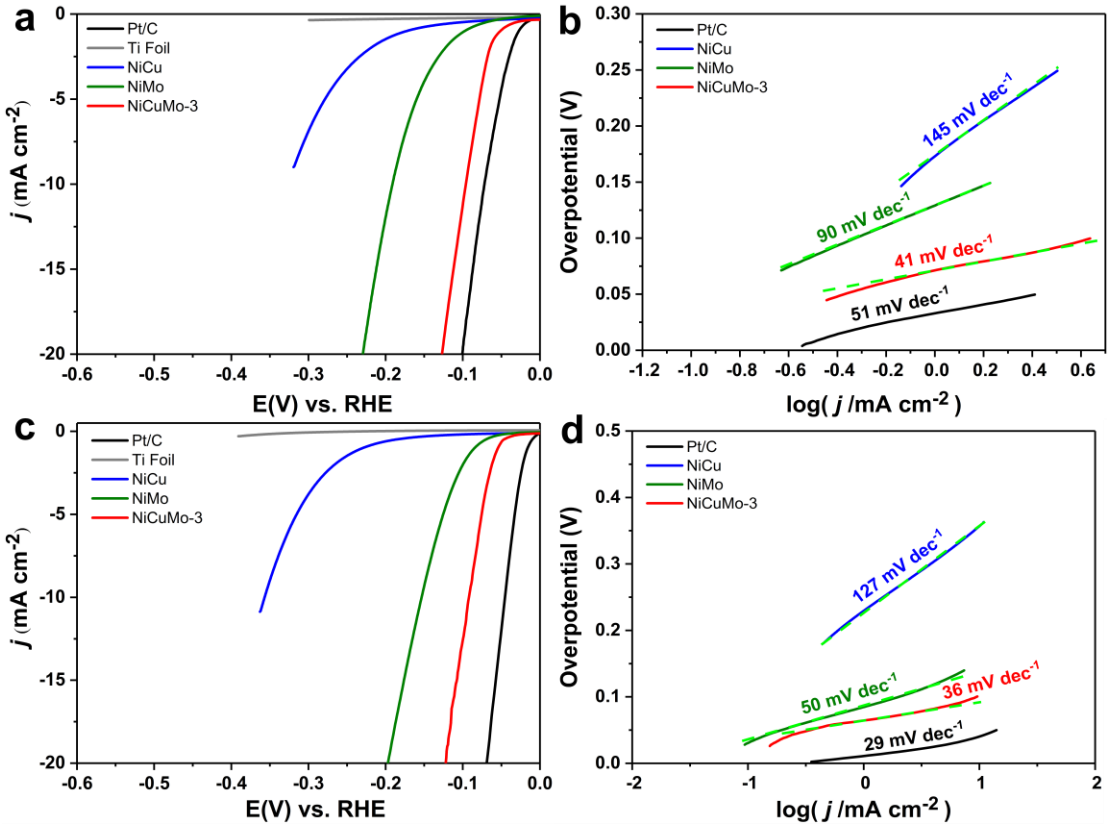

Fig. S4 Comparative LSV polarization curves for HER electrocatalytic activity in 1 M KOH (a) or in 0.5 M H_2SO_4 (c) and the corresponding Tafel plots (b or d).

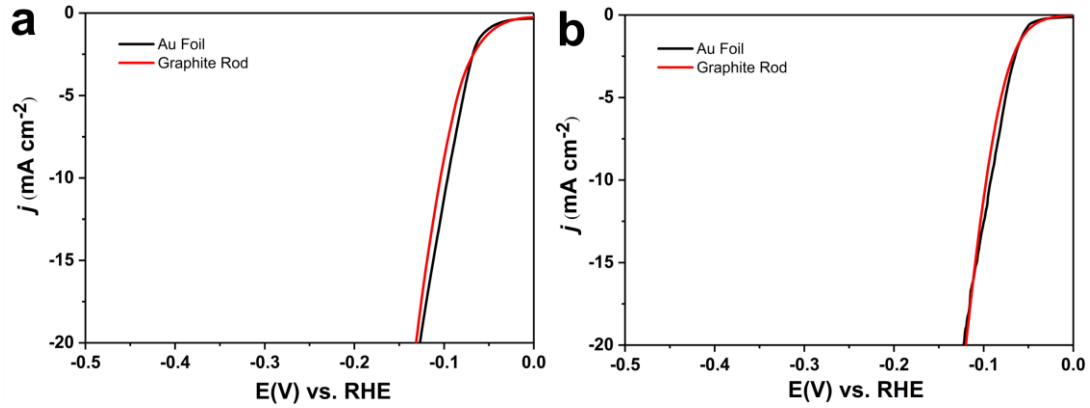

Fig. S5 Electrocatalytic HER performance comparison of NiCuMo-3 in 1 M KOH (a) or 0.5 M H_2SO_4 (b) with different counter electrodes.

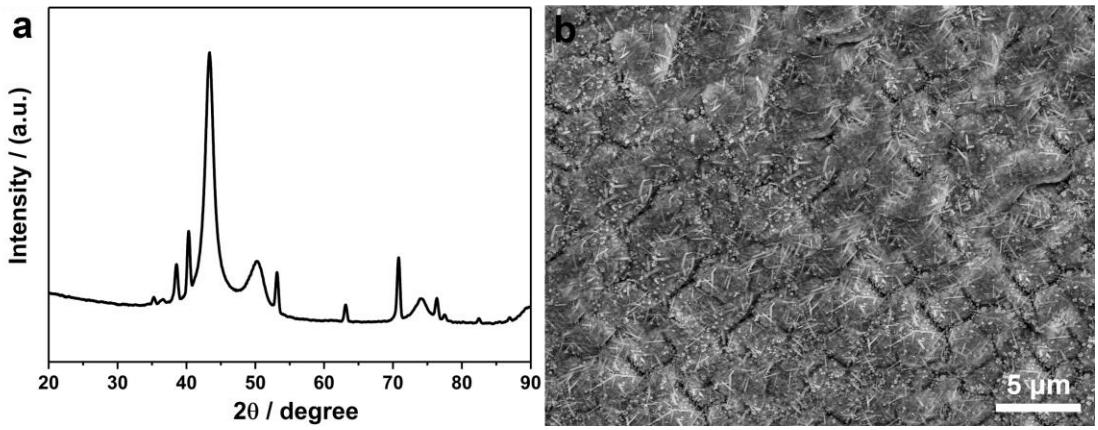

Fig. S6 The XRD pattern (a) and SEM image (b) of NiCuMo-3 after electrolysis at -100 mV vs. RHE in alkaline solution for 20 h.

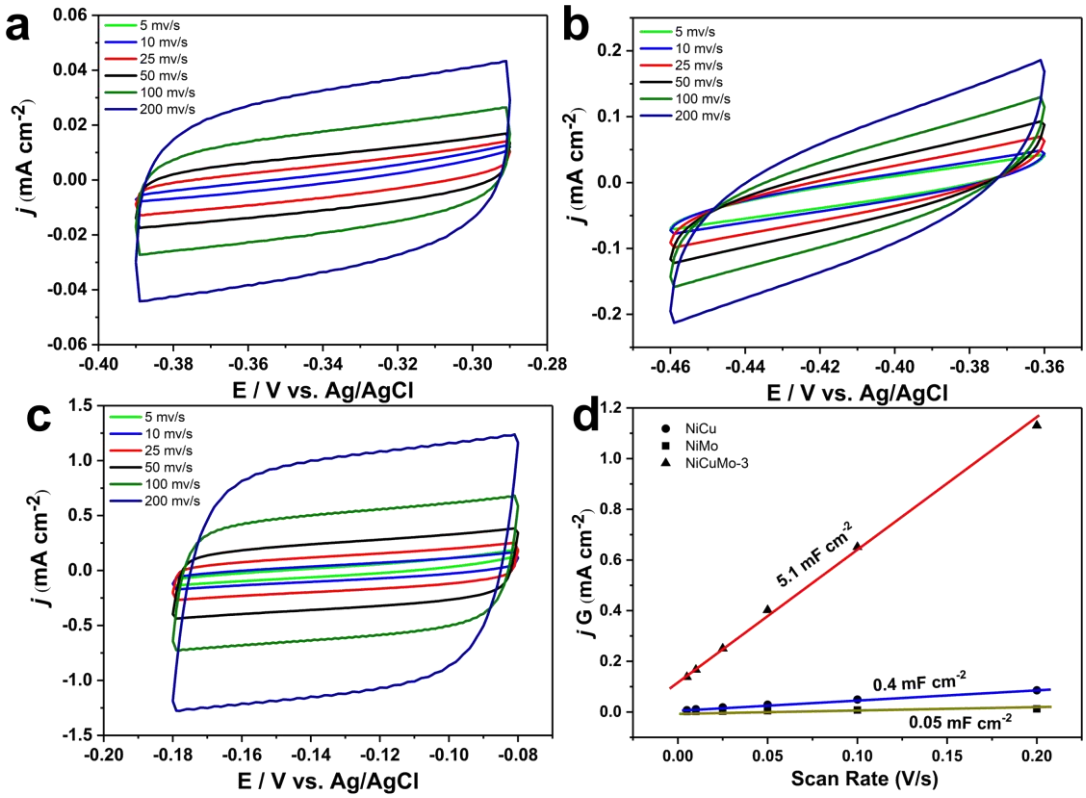

Fig. S7 Cyclic voltammograms at different scan rate from 5 mV s^{-1} to 200 mV s^{-1} in 1 M KOH. (a) NiCu, (b) NiMo, (c) NiCuMo-3 and electrochemical properties in 1 M KOH of (d) double-layer charging currents as a function of the scan rate for different electrodes.

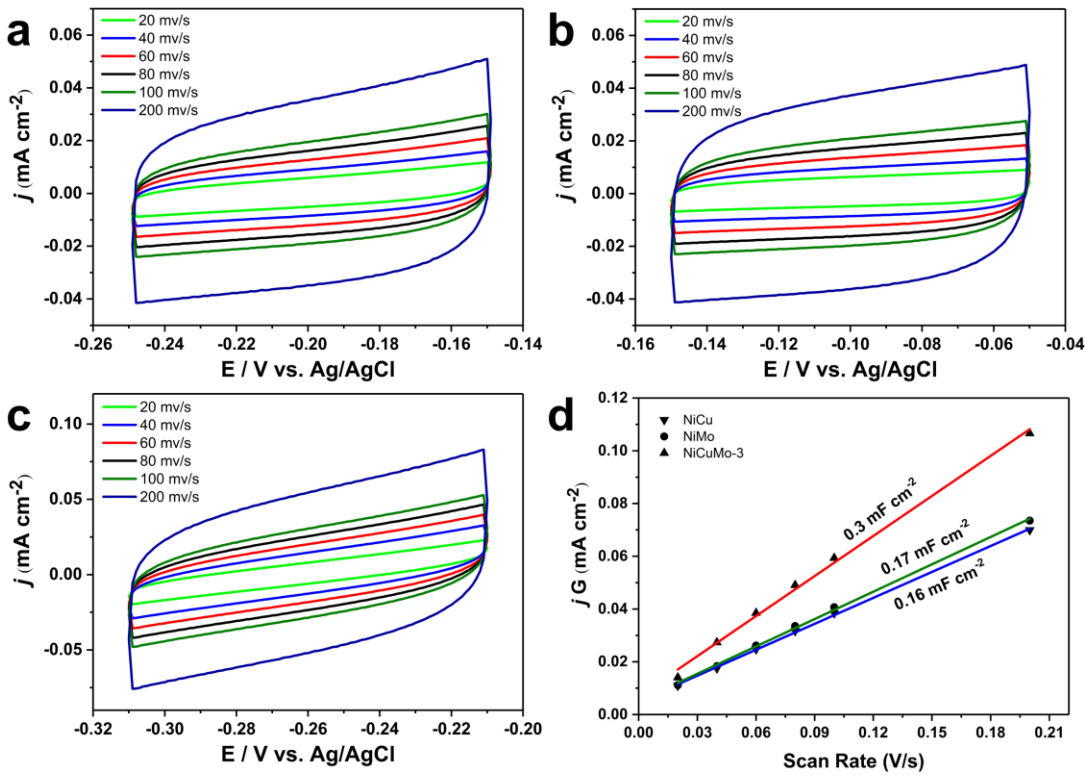

Fig. S8 Cyclic voltammograms at different scan rate from 20 mV s^{-1} to 200 mV s^{-1} in 0.5 M H_2SO_4. (a) NiCu, (b) NiMo, (c) NiCuMo-3 and electrochemical properties in 0.5 M H_2SO_4 of (d) double-layer charging currents as a function of the scan rate for different electrodes.

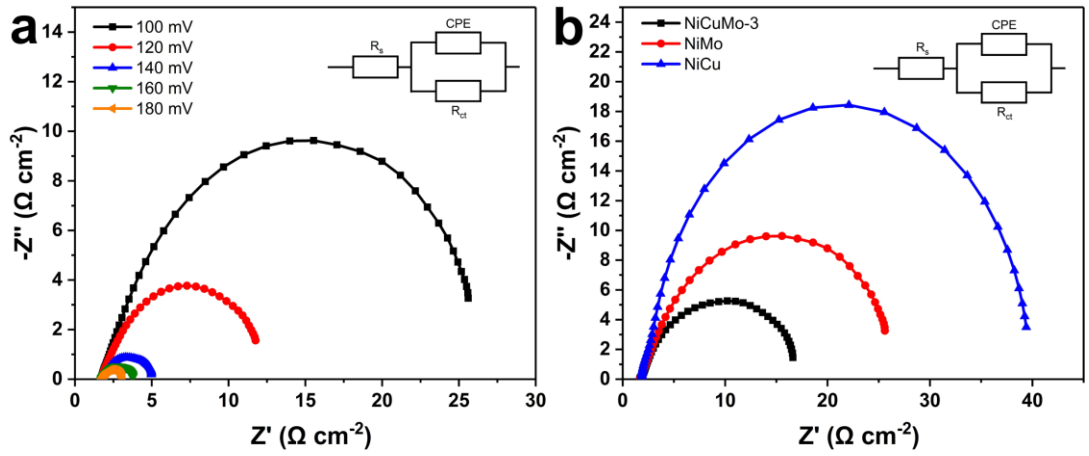

Fig. S9. (a) Nyquist plots of EIS for NiCuMo-3 at different overpotentials in 1M KOH. (b) Nyquist plots of EIS for different three catalysts at 120 mV overpotentials. (inset: the equivalent circuit of semicircles including R_S, R_{CT} and CPE).

Table S1 Comparison for HER activity in basic solutions for NiCuMo with other reported noble metal-free electrocatalysts.

Catalyst	**Electrolyte**	**Onset Potential (mV)**	**η_{10} (mV)**	**Tafel Slope (mV dec^{-1})**	**Ref**
NiCuMo-3	1 M KOH	45	95	41	This work
NiMoN/CC	1 M KOH	32	109	95	[1]
Ni_2Fe_1-Mo	1 M KOH	—	147	128	[2]
NiMo HNRs/Ti mesh	1 M KOH	60	92	76	[3]
NiMo-EDA	1 M KOH	—	72	89	[4]
NiCoMo/Ti foil	0.1 M KOH	92.6	132	108	[5]
$NiMo_2C$@C	1 M KOH	92	181	84	[6]
Ni-Mo nanopowders	1 M KOH	20	90	—	[7]
NiCu	1 M KOH	48	128	57.2	[12]
NiMoCu	6 M NaOH	40	—	200	[13]

Table S2 Comparison for HER activity in acidic solutions for NiCuMo with other reported noble metal-free electrocatalysts.

Catalyst	Electrolyte	Onset Potential (mV)	η_{10} (mV)	Tafel Slope (mV dec^{-1})	Ref
NiCuMo-3	0.5 M H_2SO_4	48	90	36	This work
NiCoMo/Ti foil	0.5 M H_2SO_4	—	35	65	[5]
$NiMo_2C$@C	0.5 M H_2SO_4	65	169	100	[6]
NiMo-NGTs	0.5 M H_2SO_4	—	65	67	[8]
$NiMoN_x$ nanosheets	0.1 M $HClO_4$	78	170	35.9	[9]
NiMoZn/Ti foil	0.5 M H_2SO_4	—	46	40	[10]
$Ni_{0.96}Mo_{0.04}S$	0.5 M H_2SO_4	170	180	46	[11]

[1] Zhang Y, Ouyang B, Xu J, 3D Porous Hierarchical Nickel–Molybdenum Nitrides Synthesized by RF Plasma as Highly Active and Stable Hydrogen-Evolution-Reaction Electrocatalysts, Advanced Energy Materials 6 (2016) 1600221.

[2] Y. Chen, C. Dong, J. Zhang, C. Zhang, Z. Zhang, Hierarchically porous Mo-doped Ni–Fe oxide nanowires efficiently catalyzing oxygen/hydrogen evolution reactions, Journal of Materials Chemistry A, 6 (2018) 8430-8440.

[3] J. Tian, N. Cheng, Q. Liu, X. Sun, Y. He, A.M. Asiri, Self-supported NiMo hollow nanorod array: an efficient 3D bifunctional catalytic electrode for overall water

splitting, Journal of Materials Chemistry A, 3 (2015) 20056-20059.

[4] Gao W, Gou W, Zhou X, Amine-Modulated/Engineered Interfaces of NiMo Electrocatalysts for Improved Hydrogen Evolution Reaction in Alkaline Solutions, Acs Applied Materials & Interfaces, 10 (2018) 1728.

[5] D. Gao, J. Guo, X. Cui, L. Yang, Y. Yang, H. He, P. Xiao, Y. Zhang, Three-Dimensional Dendritic Structures of NiCoMo as Efficient Electrocatalysts for the Hydrogen Evolution Reaction, ACS Applied Materials & Interfaces, 9 (2017) 22420-22431.

[6] X. Li, L. Yang, T. Su, X. Wang, C. Sun, Z. Su, Graphene-coated hybrid electrocatalysts derived from bimetallic metal–organic frameworks for efficient hydrogen generation, Journal of Materials Chemistry A, 5 (2017) 5000-5006.

[7] J.R. McKone, B.F. Sadtler, C.A. Werlang, N.S. Lewis, H.B. Gray, Ni–Mo Nanopowders for Efficient Electrochemical Hydrogen Evolution, ACS Catalysis, 3 (2013) 166-169.

[8] Wang T, Guo Y, Zhou Z, Ni–Mo nanocatalysts on N-doped graphite nanotubes for highly efficient electrochemical hydrogen evolution in acid, ACS nano, 10 (2016) 10397-10403.

[9] Chen W F, Sasaki K, Ma C, Hydrogen-evolution catalysts based on non-noble metal nickel–molybdenum nitride nanosheets, Angewandte Chemie International Edition, 51(2012) 6131-6135.

[10] X. Wang, R. Su, H. Aslan, J. Kibsgaard, S. Wendt, L. Meng, M. Dong, Y. Huang, F. Besenbacher, Tweaking the composition of NiMoZn alloy electrocatalyst for

enhanced hydrogen evolution reaction performance, Nano Energy, 12 (2015) 9-18.

[11] A.P. Murthy, J. Theerthagiri, K. Premnath, J. Madhavan, K. Murugan, Single-Step Electrodeposited Molybdenum Incorporated Nickel Sulfide Thin Films from Low-Cost Precursors as Highly Efficient Hydrogen Evolution Electrocatalysts in Acid Medium, The Journal of Physical Chemistry C, 121 (2017) 11108-11116.

[12] M.Y. Gao, C. Yang, Q.B. Zhang, Y.W. Yu, Y.X. Hua, Y. Li, P. Dong, Electrochemical fabrication of porous Ni-Cu alloy nanosheets with high catalytic activity for hydrogen evolution, Electrochimica Acta, 215 (2016) 609-616.

[13] Xia M, Lei T, Lv N, Synthesis and electrocatalytic hydrogen evolution performance of Ni–Mo–Cu alloy coating electrode, International Journal of Hydrogen Energy, 39(2014) 4794-4802.