Supporting Information

Facile electrochemical preparation of self-supported porous Ni-Mo alloy microsphere films as efficient bifunctional electrocatalysts for water splitting

M.Y. Gao^a, C. Yang^a, Q.B. Zhang^{a,b*}, J.R. Zeng^a, X.T. Li^a, Y.X. Hua^{a,b}, C.Y. Xu^{a,b}, P. Dong^{a,b}

^a Key Laboratory of Ionic Liquids Metallurgy, Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology. Kunming, 650093, P.R. China

^b State Key Laboratory of Complex Nonferrous Metal Resources Cleaning Utilization in Yunnan Province, Kunming 650093, China

^{*}Corresponding author. Tel: +86-871-65162008; fax: +86-871-65161278.

E-mail address: qibozhang@kmust.edu.cn (Q.B. Zhang)



Figure S1. CVs of ethaline with 0.05 M (NH₄)₆Mo₇O₂₄·4H₂O (1), 0.25 M NiCl₂·6H₂O and 0.2 M C₆H₈O₇·H₂O (2), and ethaline containing 0.25 M NiCl₂·6H₂O, 0.05 M (NH₄)₆Mo₇O₂₄·4H₂O and 0.2 M C₆H₈O₇·H₂O (3), recorded on a Pt electrode at 333 K under a scan rate of 0.02 V s⁻¹.



Figure S2. (a) EDS surveys and corresponding low- and high-magnification SEM images of the as-deposited Ni-Mo alloy films obtained at -0.95 V vs.Ag/Ag⁺ with various charge density. (b) 14 C cm⁻², (c) 28 C cm⁻², (d) 42 C cm⁻², (e) 56 C cm⁻², (f) 84 C cm⁻².



Figure S3. (a) Polarization curves of as-prepared Ni-Mo alloy films with various charge density in 1.0 M KOH solution at 298 K. Scan rate: 2 mV s⁻¹. (b) Nyquist plots of the corresponding Ni-Mo alloy films.

The deposition parameters were found to remarkably influence the composition as well as the microstructure of the resultant products (Figure. S2). To optimize the deposition condition of the Ni-Mo alloy films based on its HER catalytic activity, the deposition potential, charge density and temperature were systematically investigated. It was found that an applied potential of -0.95 V with a charge density of 56 C cm⁻² at 333 K yields the Ni-Mo alloy films with the highest HER catalytic activity, as shown in Figure. S3. A low deposition charge leads to deficient active sites, while enhanced deposition charge results in thick composite films with poor surface adhesion, which both go against the HER catalytic performance.



Figure S4. SEM images of the as-deposited Ni films/Cu (a) prepared at -0.95 V vs.Ag/Ag⁺ with 56 C cm⁻² on a Cu foil at 333 K in ethaline with 0.25 M NiCl₂·6H₂O and 0.2 M C₆H₈O₇·H₂O. (b and c are the corresponding magnified SEM images).



Figure S5. Calculated (a) HER and (b) OER exchange current densities of deposited Ni/Cu (56 C cm⁻²) and porous Ni-Mo MS/Cu (56 C cm⁻²) by applying extrapolation method to the Tafel plot.



Figure S6. Comparison of SEM of the Ni-Mo alloy films prepared at -0.95 V vs.Ag/Ag⁺ with 56 C cm⁻² before and after 24 h long-term HER (at η = -150 mV) and OER (at η = 335 mV) electrolysis in 1.0 M KOH at room temperature.



Figure S7. Comparison of EDX spectra of the Ni-Mo MS/Cu electrode prepared at -0.95 V vs.Ag/Ag⁺ with 56 C cm⁻² before and after 24 h long-term HER (at η = -150 mV) and OER (at η = 335 mV) electrolysis in 1.0 M KOH at room temperature.



Fig. S8. Comparison of XPS surveys of the Ni-Mo MS/Cu electrode prepared at -0.95 V vs.Ag/Ag⁺ with 56 C cm⁻² before and after 24 h long-term HER (at η = -150 mV) and OER (at η = 335 mV) electrolysis in 1.0 M KOH at room temperature.



Fig. S9. XPS surveys of the Ni-Mo MS/Cu electrode prepared at -0.95 V vs.Ag/Ag⁺ with 56 C cm⁻² after 24 h long-term OER (at η = 335 mV) electrolysis in 1.0 M KOH at room temperature.



Fig. S10. ICP-AES survey of Ni and Mo dissolved from the Ni-Mo MS/Cu electrode prepared at -0.95 V vs.Ag/Ag⁺ with 56 C cm⁻² during 24 h long-term OER (at η = 335 mV) electrolysis in 1.0 M KOH at room temperature.



Fig. S11. Raman spectra of the Ni-Mo MS/Cu electrode prepared at -0.95 V vs.Ag/Ag⁺ with 56 C cm⁻² before and after 24 h long-term OER (at η = 335 mV) electrolysis in 1.0 M KOH at room temperature.

Catalysts/morphology	Exchange current density (<i>i</i> ₀) /mA cm ⁻²		Overpotential at a given current density $(\eta_{ ext{given}})/ ext{mV}$		Tafel slope/ mV dec ⁻¹		Overall voltage at 10 mA cm ⁻² /V	Stability	Ref.
	HER	OER	HER	OER	HER	OER	-		
Ni-Mo alloy/porous microspheres	0.513	8.57×10 ⁻³	$\eta_{20} = 63$	$\eta_{20} = 335$	49	108	1.59	Slowly changed to 1.62 V with strong robustness for 110 h	This work
Ni ₂ P/nanoparticles	_	_	_	$\eta_{10} = 290$	_	47	1.63	Stable for 10 h	1
Ni ₂ P/microspheres	0.845	_	$\eta_{10} = 98$	$\eta_{10} = 200$	72	—	1.49	Stable for 40 h	2
Ni_5P_4 /nanosheets		Ι	$\eta_{10} = 150$	$\eta_{10} = 290$	53	_	1.70	Slowly deceased over 20 h	3
NiP/nanoparticles	_	_	$\eta_{10} = 98$	$\eta_{10} = 325$	55	120	1.68	Almost stable for 15 h	4
Ni _x P _y /nanoporous networks	_	_	$\eta_{20} = 160$	$\eta_{10} = 320$	107.3	72.2	1.57	Stable for 60 h	5
Ni_3S_2 /nanosheet arrays	_	_	$\eta_{10} = 223$	$\eta_{10} = 260$	_	_	1.76	Stable for 200 h	6
NiS/microspheres	_	_	$\eta_{20} = 158$	$\eta_{50} = 335$	83	89	1.64	Stable for 35 h	7
NiSe/nanowires	_	_	$\eta_{10} = 96$	$\eta_{20} = 270$	120	64	1.63	Slightly deceased over 20 h	8
Ni ₃ Se ₂ /microparticles		_	$\eta_{10} = 100$	$\eta_{50} = 340$	98	80	1.65	Stable for 12 h	9
Ni ₃ Se ₂ /nanoforests	0.059	_	$\eta_{10} = 203$	$\eta_{10} = 239$	79	144	1.61	Stable for 140 h	10
NiSe ₂ /nanoparticles			$\eta_{10} = 96$	$\eta_{20} = 295$	82	82	1.66	Slowly deceased over 16 h	11
NiFe/nanoparticles	0.092	5.3×10 ⁻⁷	$\eta_{10} = 219$	$\eta_{10} = 330$	111	45	1.58	Stable for 24 h	12
NiMo/hollow nanorods	_	_	$\eta_{10} = 92$	$\eta_{10} = 310$	76	47	1.64	Stable for 10 h	13
NiCo ₂ S ₄ /nanowires	_	_	$\eta_{20} = 228$	$\eta_{20} = 336$	141	89	1.68	Stable for 10 h	14
Ni-P/films	_	_	$\eta_{10} = 93$	$\eta_{10} = 334$	43	49	1.67	Slowly deceased over 24	15
NiS _x /hierarchically porous	_		$\eta_{10} = 60$	$\eta_{10} = 180$	99	96	1.47	Stable for 10 h	16

Table S1. Comparison of Ni-based bifunctional electrocatalysts in alkaline solution.

References:

- 1. L. A. Stern, L. G. Feng, F. Song, X. L. Hu, Energ. Environ. Sci., 2015, 8, 2347.
- 2. B. You, N. Jiang, M. L. Sheng, M. W. Bhushan, Y. J. Sun, ACS Catal., 2016, 6, 714.
- 3. M. Ledendecker, S. K. Calderon, C. Papp, H. P. Steinruck, M. Antonietti, M. Shalom, Angew. Chem., 2015, 127, 12538.
- 4. Q. Liu, S. Gu, C. M. Li, J. Power Sources, 2015, 299, 342.
- 5. J. Y. Li, J. Li, X. M. Zhou, Z. M. Xia, W. Gao, Y. Y. Ma, Y. Q. Qu, ACS Appl. Mater. Inter., 2016, 8, 10826.
- 6. L. L. Feng, G. T. Yu, Y. Y. Wu, G. D. Li, H. Li, Y. H. Sun, T. Asefa, W. Chen, X. X. Zou, J. Am. Chem. Soc., 2015, 137, 14023.
- 7. W. X. Zhu, X. Y. Yue, W. T. Zhang, S. X. Yu, Y. H. Zhang, J. Wang, J. L. Wang, Chem. Commun., 2016, 52, 1486.
- 8. C. Tang, N. Y. Cheng, Z. H. Pu, W. Xing, X. P. Sun, Angew. Chem. Int. Edit., 2015, 54, 9351.
- 9. J. Shi, J. Hu, Y. Luo, X. Sun, A. M. Asiri, *Catal. Sci. Technol.*, 2015, 5, 4954.
- 10. R. Xu, R. Wu, Y. M. Shi, J. F. Zhang, B. Zhang, *Nano Energy*, 2016, **24**, 103.
- 11. Z. H. Pu, Y. L. Luo, A. M. Asiri, X. P. Sun, ACS Appl. Mater. Inter., 2016, 8, 4718.
- 12. X. Zhang, H. M. Xu, X. X. Li, Y. Y. Li, T. B. Yang, Y. Y. Liang, ACS Catal., 2016, 6, 580.
- 13. J. Q. Tian, N. Y. Cheng, Q. Liu, X. P. Sun, Y. Q. He, A. M. Asiri, J. Mater. Chem. A, 2015, 3, 20056.
- 14. D. N. Liu, Q. Lu, Y. L. Luo, X. P. Sun, A. M. Asiri, *Nanoscale*, 2015, 7, 15122.
- 15. N. Jiang, B. You, M. Sheng, Y. Sun, *ChemCatChem*, 2016, **8**, 106.
- 16. B. You, Y. Sun, Adv. Energy Mate., 2016, 6, 1502333