

Electronic Supplementary Information (ESI)

**Free standing porous Co/Mo architecture as robust bifunctional catalyst
toward water splitting**

Yuxuan Li,^b Xingbo Ge,^{a, b} Leidanyang Wang,^b Jia Liu,^b Yong Wang^b and Lanxiang Feng^b*

^a State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest

Petroleum University, Chengdu 610500, P. R. China

^b The Center of New Energy Materials and Technology, School of Chemistry and Chemical

Engineering, Southwest Petroleum University,

Chengdu 610500, China

* Corresponding author:

E-mail: xbge@swpu.edu.cn; Tel: +86-28-83037337; Fax: +86-28-83037337.

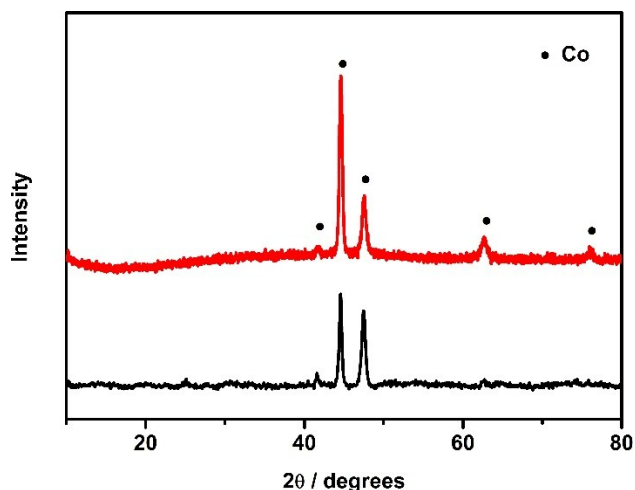


Figure S1. X-ray diffraction (XRD) patterns of Co sheet (black) and etched Co (red).

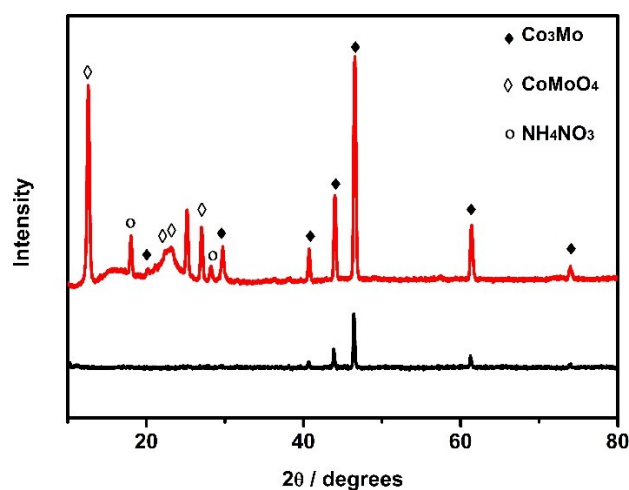


Figure S2. X-ray diffraction (XRD) patterns of as-prepared Co_3Mo ribbon (black) and etched Co/Mo (red).

An X-ray diffractometer (PANalytical B.V.), configured with a $\text{Cu-K}\alpha$ radiation source, graphite monochromator, and scintillation counter, was used to investigate the catalysts' crystalline structures. For etched Co sheet (Figure S1, red), all the detectable diffraction peaks (occur at 41.7° , 44.6° , 47.5° , 62.7° , and 76.0°) are identical to the reported experimental patterns of hexagonal metallic cobalt (JCPDF 01-089-7373). No clear signal for cobalt oxides is discovered after soaking in CAN according to XRD patterns, suggesting an amorphous CoO_x thin film on the etched Co surface. Peaks detected at 20.2° , 29.7° , 40.8° , 44.0° , 46.5° ,

61.3° and 73.9° for etched Co/Mo could be derived from the hexagonal Co₃Mo alloy (JCPDF 029-0488), while peaks at 12.6°, 22.5°, 23.3°, 27.0° are assigned to the cobalt molybdenum oxide with the formula of CoMoO₄ or MoO₃·CoO ((JCPDF 015-0439), indicating that some of the surface atoms of Co₃Mo have been transformed to oxidation states of Co^{II} and Mo^{III} respectively. Peaks at 28.2° could be ascribed to the trace amounts of tetragonal ammonium nitrate NH₄NO₃ (JCPDF 009-0132), which might be originated from Ce(NH₄)₂(NO₃)₆.

Table S1. Comparison of some reported non-noble-metal OER catalysts in basic electrolyte.

Catalyst	Electrolyte	η_{onset} (mV)	$\eta @ 10 \text{ mA cm}^{-2}$ (mV)	Tafel slope (mV dec ⁻¹)	Ref.
etched Co/Mo	0.1 M KOH	270	470	123	this work
Co ₃ Mo	0.1 M KOH	340	530	87	this work
etched Co	0.1 M KOH	311	N/A	132	this work
Co sheet	0.1 M KOH	356	N/A	113	this work
NA-NiCo ₂ O ₄	1 M NaOH	N/A	458	52	[1]
Ni(OH) ₂	0.1 M KOH	350	595	165	[2]
MWCNTs + Ni(OH) ₂	0.1 M KOH	337	540	140	[2]
MWCNTs/Ni(OH) ₂	0.1 M KOH	322	474	87	[2]
<i>meso</i> Co ₃ O ₄ -35	0.1 M KOH	N/A	636	N/A	[3]
<i>meso</i> Co ₃ O ₄ -100	0.1 M KOH	N/A	525	N/A	[3]
Fe-doped <i>meso</i> Co ₃ O ₄	0.1 M KOH	N/A	486	N/A	[4]

Table S2. Comparison of some reported Pt-free HER catalysts in basic electrolyte.

Catalyst	Electrolyte	η_{onset} (mV)	$\eta @ 10 \text{ mA}$ cm^{-2} (mV)	Tafel slope (mV dec^{-1})	Ref.
etched Co/Mo	1 M KOH	90	240	139	this work
Co ₃ Mo	1 M KOH	256	340	105	this work
Mo sheet	1 M KOH	260	370	97	this work
Ni wire	1 M NaOH	N/A	350	N/A	[6]
Ni/Ti	1 M NaOH	N/A	220	N/A	[6]
Co-P compact film	1 M KOH	N/A	>400	N/A	[7]
porous Co-P/Co-PO ₄	1 M KOH	N/A	380	N/A	[7]
Ni-P	1 M NaOH	N/A	>300	125	[10]
Ni(OH) ₂ /NF	1 M NaOH	120	250	N/A	[14]
MoB	1 M KOH	140	220	59	[11]
CoO _x @CN	1 M KOH	85	232	115	[13]
Mo ₂ C	1 M KOH	140	270	78	[15]
WN nanorod array	1 M KOH	200	285	170	[16]
NiMo ₃ S ₄	0.1 M KOH	59	257	98	[12]

Table S3. Comparison of some reported Pt-free HER catalysts in acidic electrolyte.

Catalyst	Electrolyte	η_{onset} (mV)	$\eta @ 10 \text{ mA cm}^{-2}$ (mV)	Tafel slope (mV dec ⁻¹)	Ref.
etched Co/Mo	0.5 M H ₂ SO ₄	109	220	71	this work
Co ₃ Mo	0.5 M H ₂ SO ₄	130	390	113	this work
Mo sheet	0.5 M H ₂ SO ₄	240	N/A	76	this work
Co-NRCNTs	0.5 M H ₂ SO ₄	N/A	260	69	[5]
C ₃ N ₄ @NG	0.5 M H ₂ SO ₄	N/A	240	52	[8]
NENU-500	0.5 M H ₂ SO ₄	180	237	96	[9]
MoO ₃ -MoS ₂	1.0 M H ₂ SO ₄	150-200	300	50-60	[17]
MoS ₂ NF/GR	0.5 M H ₂ SO ₄	190	N/A	95	[18]
MoS ₂ AG/rGO	0.5 M H ₂ SO ₄	290	N/A	102	[23]
MoN/C	0.5 M H ₂ SO ₄	157	N/A	55	[19]
MoS ₂ /CNT-GR	0.5 M H ₂ SO ₄	140	255	100	[20]
Mo ₂ N/CNT-GR	0.5 M H ₂ SO ₄	118	186	72	[20]
MoS ₂ /Mo	0.5 M H ₂ SO ₄	150-200	~280-290	50-72	[21]
MoS ₂ /MoO ₂	0.5 M H ₂ SO ₄	104	240	76.1	[22]
[Mo ₃ S ₄] ⁴⁺	0.5 M H ₂ SO ₄	150	280	120	[23]
MoS ₂ NS/GR	0.5 M H ₂ SO ₄	~140	N/A	41	[24]
exfoliated WS ₂	0.5 M H ₂ SO ₄	280	N/A	110	[25]
MoS ₂	0.5 M H ₂ SO ₄	180	270	50	[26]
Co _{0.6} Mo _{1.4} N ₂	0.1 M HClO ₄	N/A	200	N/A	[27]

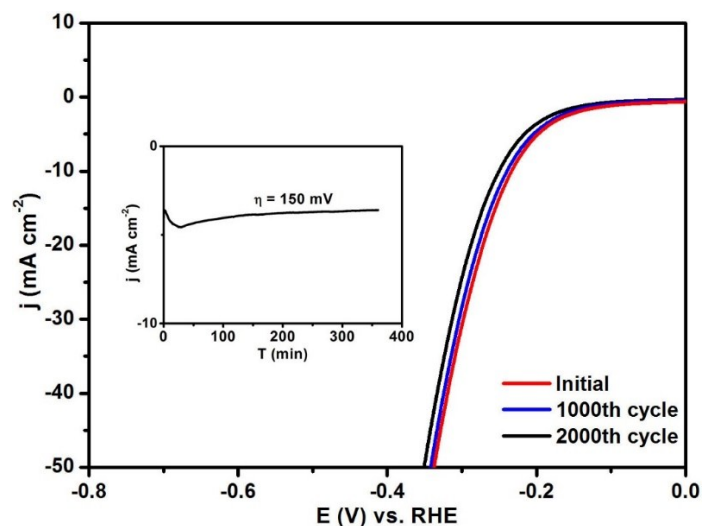


Figure S3. HER polarization curves of the etched Co/Mo before and after 1000 and 2000 cycles in 1 M KOH. Inset is the chronopotentiometry curve of the etched Co/Mo at an overpotential of 150 mV.

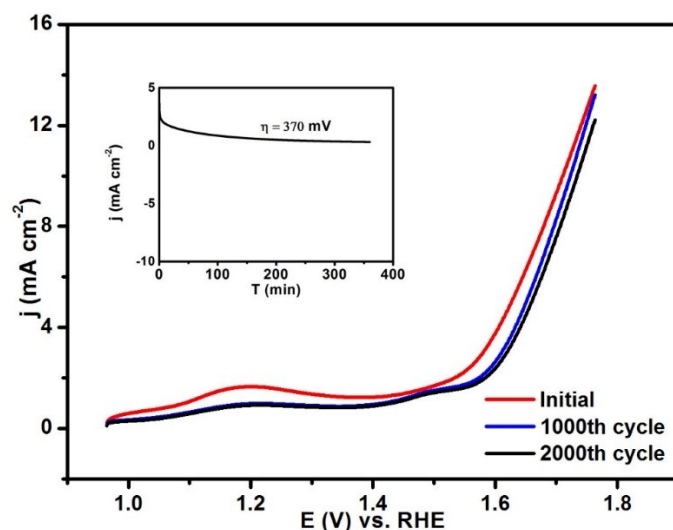


Figure S4. OER polarization curves of the etched Co/Mo before and after 1000 and 2000 cycles in 0.1 M KOH. Inset is the chronopotentiometry curve of the etched Co/Mo at 1.60 V vs. RHE.

References

- [1] J. Wang, T. Qiu, X. Chen, Y. Lu, W. Yang, *J. Power Sources*, 2014, **268**, 341-348.
- [2] X. Zhou, Z. Zhang, Y. Ma, Y. Qu, *J. Mater. Chem. A*, 2014, **2**, 11799-11806.
- [3] H. Tüysüz, Y. J. Hwang, S. B. Khan, A. M. Asiri, P. Yang, *Nano Res.*, 2013, **6(1)**, 47-54.
- [4] T. Grewe, X. Deng, H. Tüysüz, *Chem. Mater.* 2014, **26**, 3162-3168.
- [5] X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, *Angew. Chem. Int. Ed.* 2014, **53**, 4372-4376.
- [6] J. R. McKone, B. F. Sadtler, C. A. Werlang, N. S. Lewis, H. B. Gray, *ACS Catal.*, 2013, **3**, 166-169.
- [7] Y. Yang, H. Fei, G. Ruan, J. M. Tour, *Adv. Mater.*, 2015, **27**, 3175-3180.
- [8] Y. Zheng, Y. Jiao, Y. Zhu, L. H. Li, Y. Han, Y. Chen, A. Du, M. Jaroniec, S. Z. Qiao, *Nat. Commun.* 2014, **5**, 3783-3790.
- [9] J. Qin, D. Du, W. Guan, X. Bo, Y. Li, L. Guo, Z. Su, Y. Wang, Y. Lan, H. Zhou, *J. Am. Chem. Soc.*, 2015, **137**, 7169-7177.
- [10] L. Wan, J. Zhang, Y. Chen, C. Zhong, W. Hu, Y. Deng, *J. Mater. Sci.*, 2017, **52**, 804-814.
- [11] H. Vrubel, X. Hu, *Angew. Chem. Int. Ed.*, 2012, **51**, 12703-12706.
- [12] J. Jiang, M. Gao, W. Sheng, Y. Yan, *Angew. Chem. Int. Ed.*, 2016, **55**, 15240-15245.
- [13] H. Jin, J. Wang, D. Su, Z. Wei, Z. Pang, Y. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 2688-2694.
- [14] J. Luo, J. H. Im, M. T. Mayer, M. Schreier, M. K. Nazeeruddin, N. G. Park, S. D. Tilley, H. J. Fan, M. Grätzel, *Science*, **345**, 1593-1596.
- [15] C. G. Morales-Guio, K. Thorwarth, B. Niesen, L. Liardet, J. Patscheider, C. Ballif, X. Hu, *J. Am. Chem. Soc.*, 2015, **137**, 7035-7038.
- [16] J. Shi, Z. Pu, Q. Liu, A. M. Asiri, J. Hu, X. Sun, *Electrochim. Acta*, 2015, **154**, 345-351.
- [17] Z. Chen, D. Cummins, B. N. Reinecke, E. Clark, M. K. Sunkara, T. F. Jaramillo, *Nano Lett.*, 2011, **11**, 4168-4175.
- [18] C. Ma, X. Qi, B. Chen, S. Bao, Z. Yin, X. Wu, Z. Luo, J. Wei, H. Zhang, H. Zhang, *Nanoscale*, 2014, **6**, 5624-5629.
- [19] W. Chen, K. Sasaki, C. Ma, A. I. Frenkel, N. Marinkovic, J. T. Muckerman, Y. Zhu, R. R. Adzic, *Angew. Chem. Int. Ed.*, 2012, **51**, 6131-6135.
- [20] D. H. Youn, S. Han, J. Y. Kim, J. Y. Kim, H. Park, S. H. Choi, J. S. Lee, *ACS Nano*, 2014, **8**, 5164-517.
- [21] Y. Yang, H. Fei, G. Ruan, C. Xiang, J. M. Tour, *Adv. Mater.*, 2014, **26**, 8163-8168.
- [22] L. Yang, W. Zhou, D. Hou, K. Zhou, G. Li, Z. Tang, L. Lia, S. Chen, *Nanoscale*, 2015, **7**, 5203-5208.

- [23] T. F. Jaramillo, J. Bonde, J. Zhang, Bee-Lean Ooi, K. Andersson, J. Ulstrup, I. Chorkendorff, *J. Phys. Chem. C*, 2008, **112**, 17492-17498.
- [24] X. Zheng, J. Xu, K. Yan, H. Wang, Z. Wang, S. Yang, *Chem. Mater.*, 2014, **26**, 2344-2353.
- [25] J. Kim, S. Byun, A. J. Smith, J. Yu, J. Huang, *J. Phy. Chem. Lett.*, 2013, **4**, 1227-1232.
- [26] J. Kibsgaard, Z. Chen, B. N. Reinecke, T. F. Jaramillo, *Nat. Mater.*, 2012, **11**, 963-969.
- [27] B. Cao, G. M. Veith, J. C. Neuefeind, R. R. Adzic, P. G. Khalifah, *J. Am. Chem. Soc.*, 2013, **135**, 19186-19192.