

Supporting Information for Publication

Oxygen Vacancy Enriched NiMoO₄ Nanorods via Microwave heating: a Promising highly stable Electrocatalyst for Total Water Splitting

*Arun Karmakar^{†‡}, Kannimuthu Karthick^{†‡}, Selvasundarasekar Sam Sankar,^{†‡} Sangeetha
Kumaravel^{†‡}, Madhu Rangunath^{†‡} and Subrata Kundu^{†‡*}*

[†]*Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India.*

[‡]*Electrochemical Process Engineering (EPE) Division, CSIR-Central Electrochemical
Research Institute (CECRI), Karaikudi-630003, Tamil Nadu, India.*

*To whom correspondence should be addressed, *E-mail:* skundu@cecri.res.in;
kundu.subrata@gmail.com, Phone/Fax: (+ 91) 4565-241487.

This file contains 11 pages in which the details of reagents, methods of synthesis, electrochemical characterizations, electrochemical results, FE-SEM.

No. of Figures: 6

No. Tables: 1

Reagents, Instruments and electrochemical characterization

Nickel chloride (NiCl_2), sodium molybdate (Na_2MoO_4) and sodium borohydride (NaBH_4) were purchased from Sigma-Aldrich and used as received. Ni foam was procured from Sigma-Aldrich and used after surface cleaning. All the electrochemical characterizations were carried out by using conventional three electrode system with carbon cloth as a counter electrode and Hg/HgO as a reference electrode. CV curves were taken at a scan rate of 5 mV/s and all the data were 50% iR corrected by manually. Accelerated degradation studies were carried out at scan rate of 200 mV/s for 1000 cycles to know the stability of the catalyst at the interface at an accelerated condition. Chronoamperometric study was carried at overpotentials for 12 h that could drive 50 mA/cm² without iR correction. Electrochemical impedance spectroscopy (EIS) analyses were carried out at a frequency range from 0.1 Hz to 100 KHz with amplitude of 0.01 V at the onset overpotential. The potential scales all polarization curves were converted into reversible hydrogen electrode (RHE) scale following literature reports for ease of evaluation and comparison of the activity of our catalyst systems. DI water was used throughout entire experiments. The as prepared catalysts with different stoichiometric ratios were characterized with HR-TEM, (TecnaiTM G² TF20) working at an accelerating voltage of 200 kV and by Talos F-200-S with HAADF elemental mapping. Colour mapping and Energy Dispersive X-ray Spectroscopy (EDS) analysis were carried out with the FESEM instrument with the images (SUPRA 55VP Carl Zeiss) with a separate EDS detector connected to that instrument. Scanning Electron Microscopy (SEM) analysis was carried with a Hitachi, Japan make model S-3000H instrument having magnification 30X to 300 KX with the accelerating voltage ~ 0.3 to 30 kV. The XRD analysis carried out with a scanning rate of 5° min⁻¹ in the 2 θ range 10-90° using a Rigaku X-ray powder diffractometer (XRD) with Cu K α radiation ($\lambda = 0.154$ nm). X-ray photoelectron spectroscopic (XPS) analysis was performed using a Theta Probe AR-XPS system (Thermo Fisher Scientific, UK).

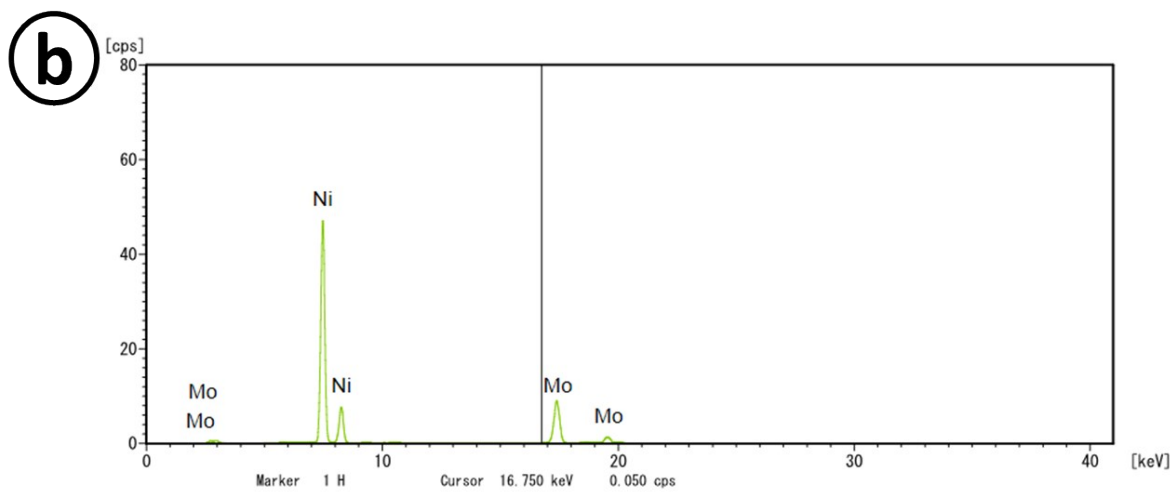
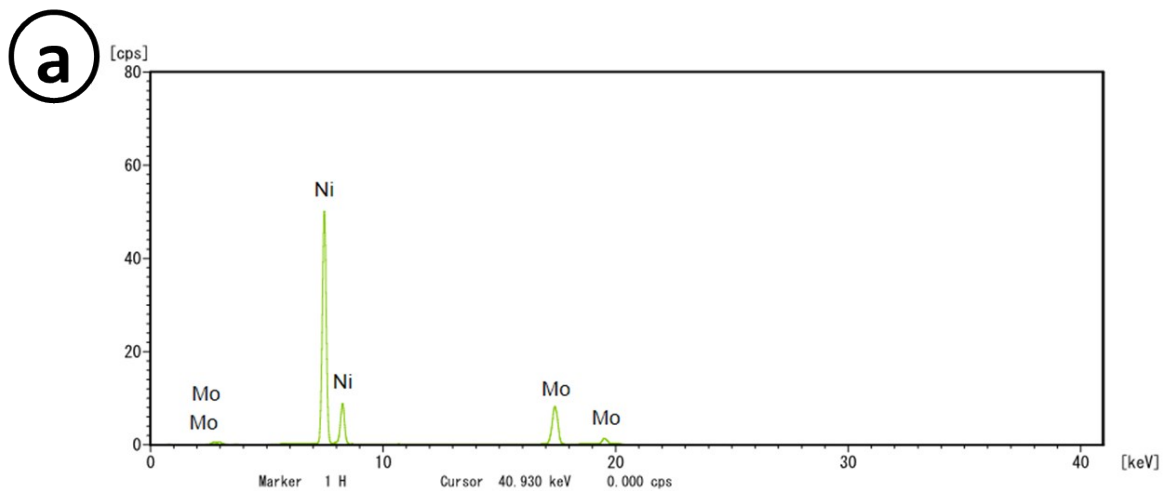


Figure S1: (a) XRF spectrum of NiMoO_4 ; (b) XRF spectrum of $\text{NiMoO}_4(\text{V}_o)$.

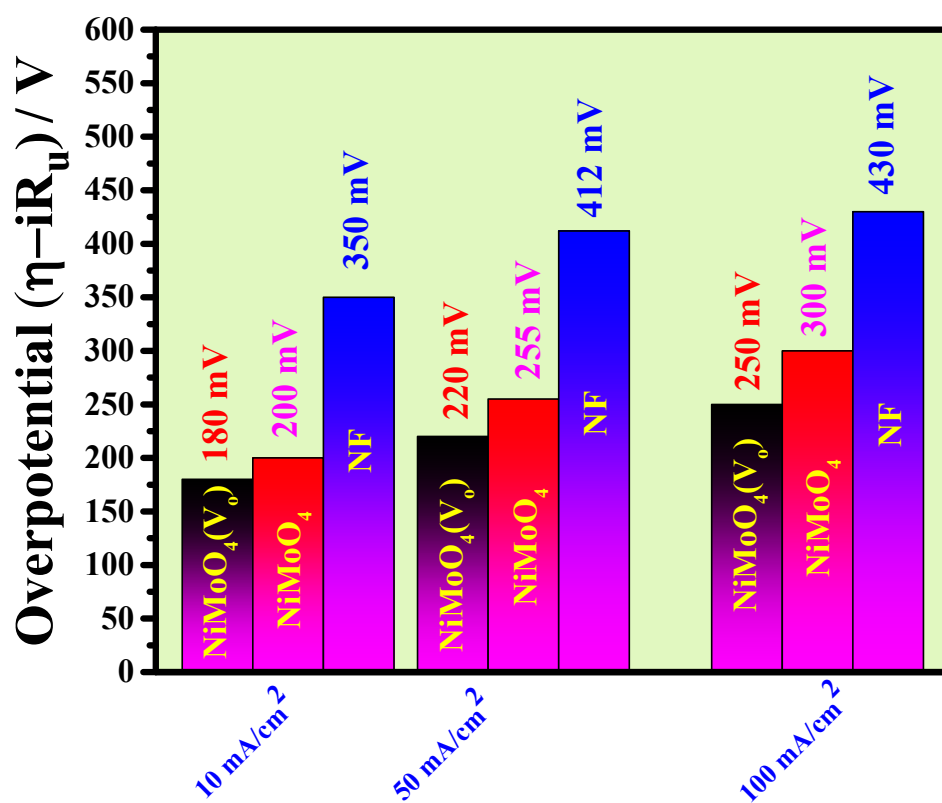


Figure S2: Representation of required overpotentials to reach different current density in OER via bar diagram.

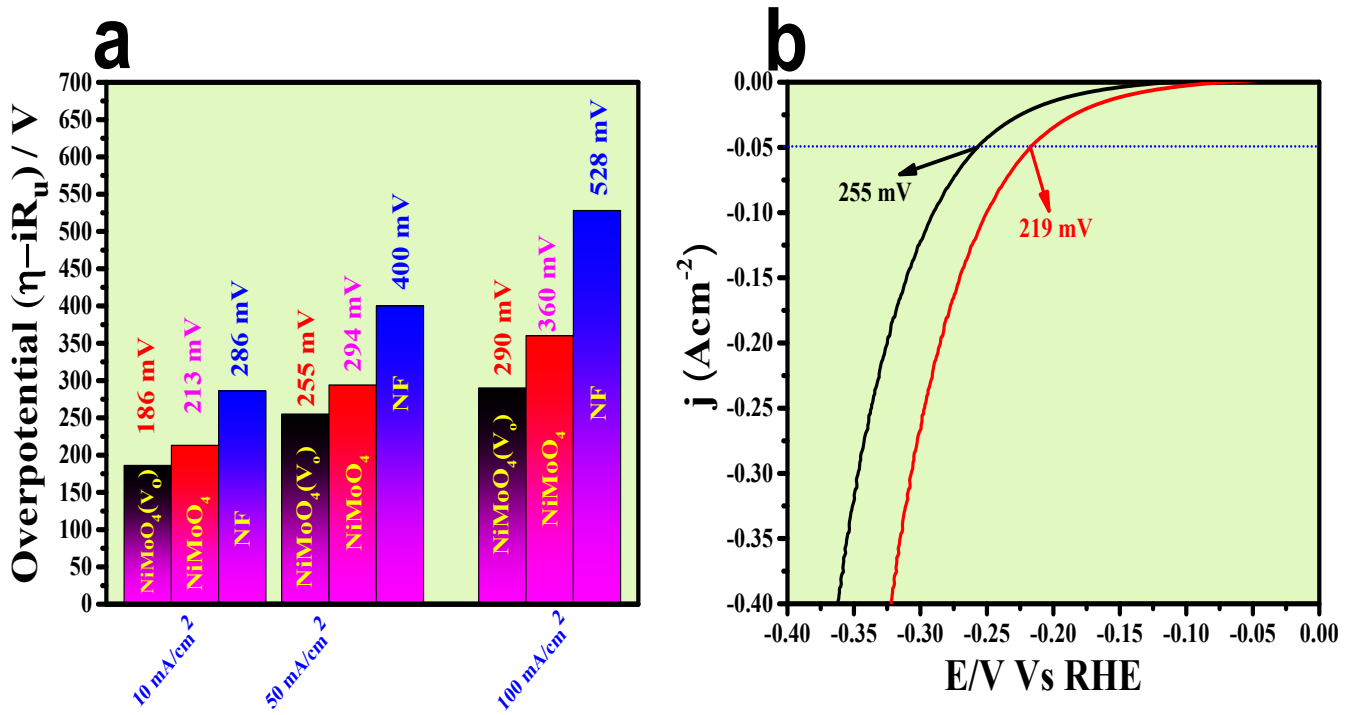


Figure S3: (a) Bar diagram corresponding to different overpotentials required for certain current density in HER, (b) LSV curve of HER before and after the cycling at a high scan rate.

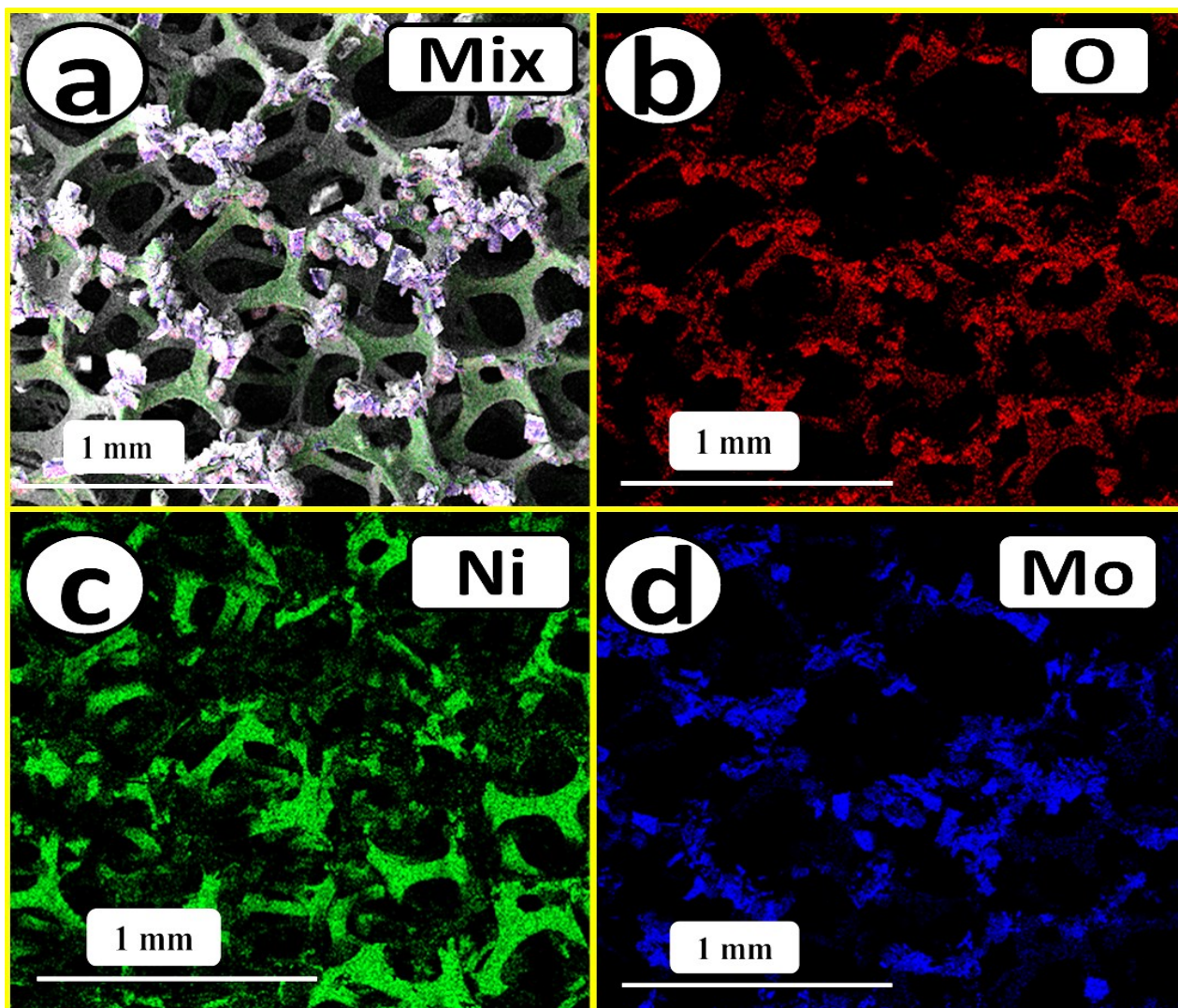


Figure S4: (a-d) Post OER colour mapping outcomes of different elements in FESEM mode.

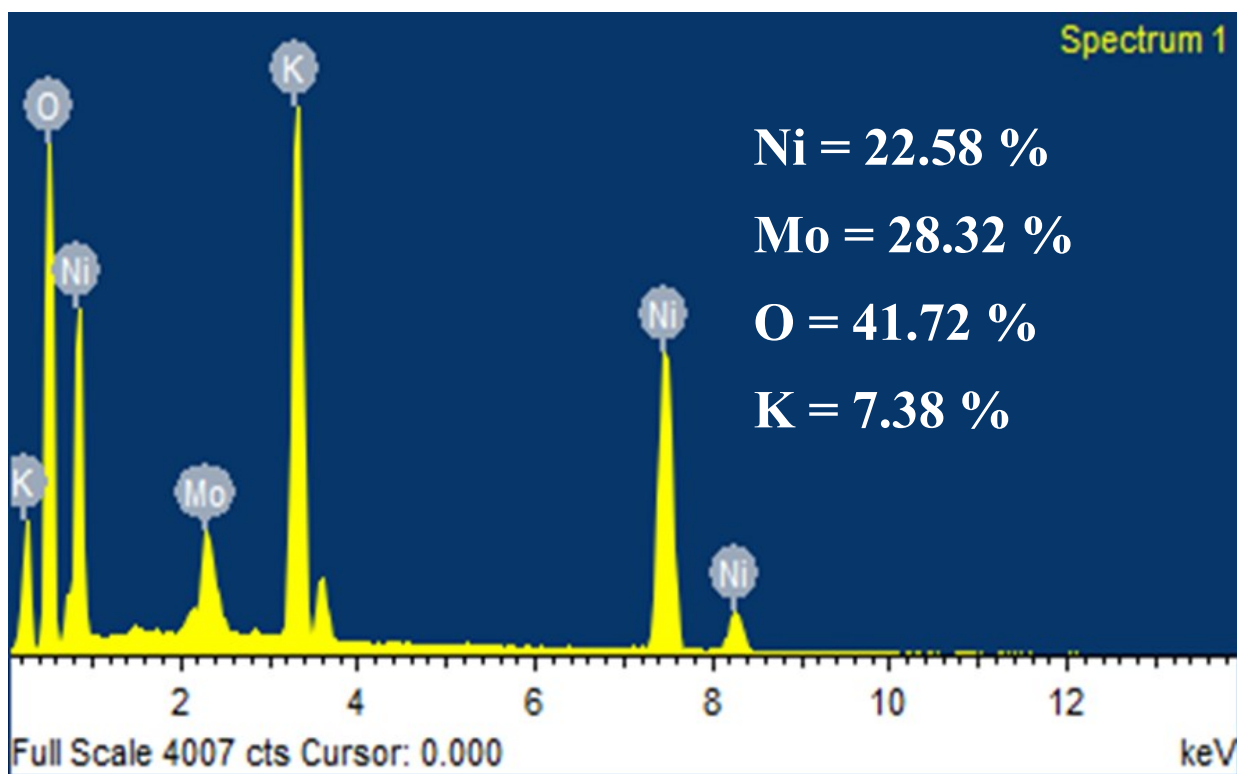


Figure S5: Post OER EDS spectrum of different elements in FESEM mode.

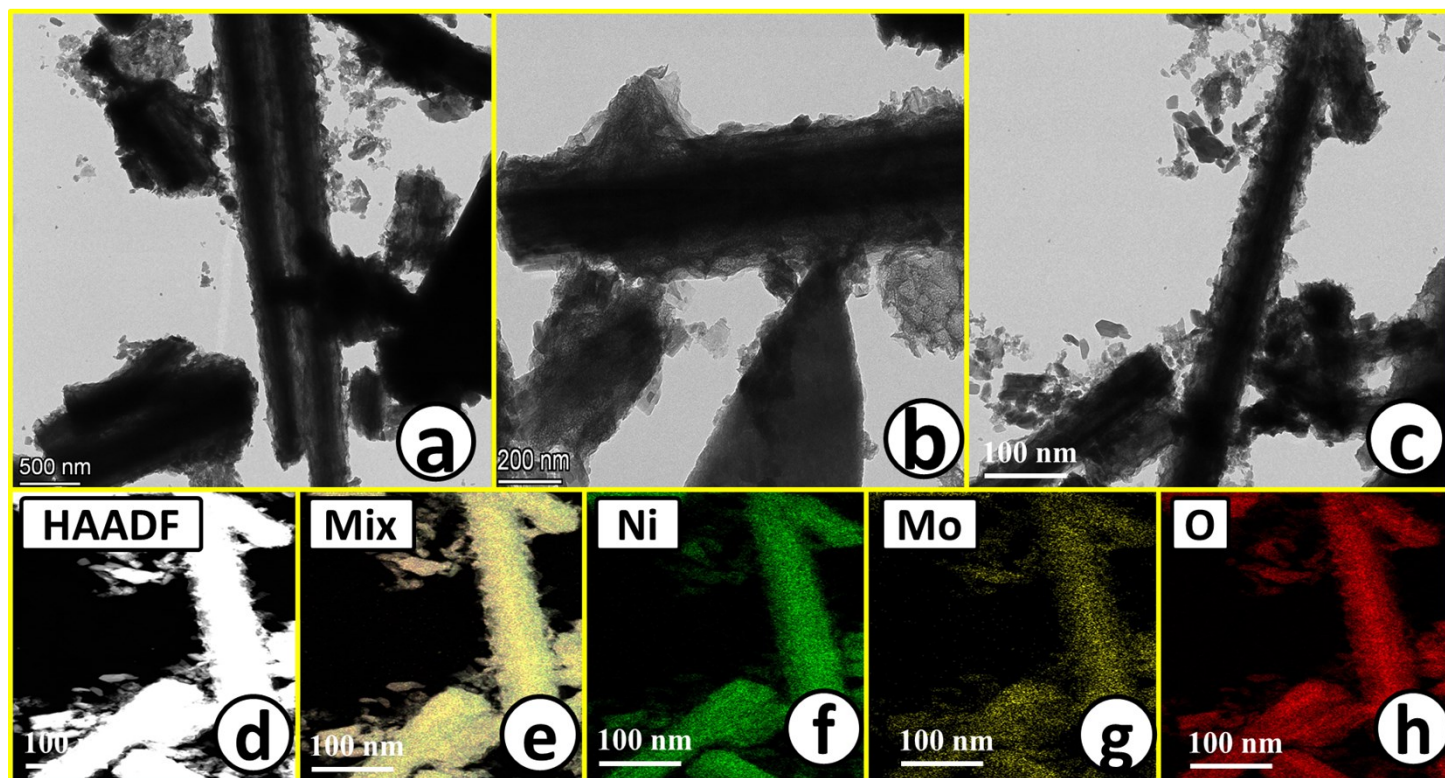


Figure S6: (a-c) Low to high magnification HR-TEM images of NiMoO₄(V_o) after the degradation study, (d) is the HAADF image of rod-like NiMoO₄ taken for the mapping analysis and (e-h) are the characteristic mapping results of mix, Ni K, Mo K, O K and respectively.

Sl. No.	Catalysts	Overpotential (mV)	Tafel Slope (mV/dec)	Ref.
1	NiMoO ₄ derived NiMoFeO@NC	270@ 50 mA/cm ²	66.6	1
2	Ni(OH) ₂ Nanosheet on CoMoO ₄	349@ 100mA/cm ²	67.6	2
3	Self-supported NiMo-based nanowire	230@ 10 mA/cm ²	116	3
4	NiMoO _{4-x} /MoO ₂	233@ 10mA/cm ²	69	4
5	NiCo ₂ O ₄ @CoMoO ₄ /NF	265@ 20mA/cm ²	102	5
6	CoMoO ₄ nanosheets	314@ 10mA/cm ²	51	6
7	Hierarchical CoMoO ₄ nanoparticle	317@ 100mA/cm ²	119	7
8	Oxygen vacancy enriched CoMoO ₄	309@ 10mA/cm ²	-	8
9	Hybrid-atom-doped NiMoO ₄ nanotubes	217@ 10mA/cm ²	90	9
10	NiCo ₂ O ₄ @NiMoO ₄	250@ 10mA/cm ²	58.7	10
11	Spinel CoMoO ₄	263@ 10mA/cm ²	87	11
12	One-dimensional CoMoO ₄ nanorods	343@ 10mA/cm ²	67	12
13	Nanostructured NiMoO ₄	340@ 10mA/cm ²	45.6	13
14	CoOOH derived CoMoO ₄	274@ 10mA/cm ²	66	14
15	Post phospharization derived NiMoO ₄	370@ 5mA/cm ²	70.3	15
16	Oxygen vacancy enriched NiMoO ₄	180@ 10mA/cm ² 220@ 50mA/cm ² 250@ 100mA/cm ²	30	This work

Table S1: Comparative OER activity of our catalyst with recently reported similar types of catalysts.

References

- 1 Y. Wang, Y. Zhu, S. Zhao, S. She, F. Zhang, Y. Chen, T. Williams, T. Gengenbach, L. Zu, H. Mao, W. Zhou, Z. Shao, H. Wang, J. Tang, D. Zhao and C. Selomulya, *Matter*, 2020, **3**, 2124–2137.
- 2 Y. Xu, L. Xie, D. Li, R. Yang, D. Jiang and M. Chen, *ACS Sustain. Chem. Eng.*, 2018, **6**, 16086–16095.
- 3 Y. Wang, Y. Sun, F. Yan, C. Zhu, P. Gao, X. Zhang and Y. Chen, *J. Mater. Chem. A*, 2018, **6**, 8479–8487.
- 4 Z. Zhang, X. Ma and J. Tang, *J. Mater. Chem. A*, 2018, **6**, 12361–12369.
- 5 Y. Gong, Z. Yang, Y. Lin, J. Wang, H. Pan and Z. Xu, *J. Mater. Chem. A*, 2018, **6**, 16950–16958.
- 6 H. Jiang, Z. Cui, C. Xu and W. Li, *Chem. Commun.*, 2019, **55**, 9432–9435.
- 7 X. Guan, L. Yang, G. Zhu, H. Wen, J. Zhang, X. Sun, H. Feng, W. Tian, X. Chen and Y. Yao, *Sustain. Energy Fuels*, 2020, **4**, 1595–1599.
- 8 K. Chi, X. Tian, Q. Wang, Z. Zhang, X. Zhang, Y. Zhang, F. Jing, Q. Lv, W. Yao, F. Xiao and S. Wang, *J. Catal.*, 2020, **381**, 44–52.
- 9 Z. Yin, S. Zhang, W. Chen, M. Xinzhi, Y. Zhou, Z. Zhang, X. Wang and J. Li, *New J. Chem.*, 2020, **44**, 17477–17482.
- 10 X. Du, J. Fu and X. Zhang, *ChemCatChem*, 2018, **10**, 5533–5540.
- 11 B. Fei, Z. Chen, Y. Ha, R. Wang, H. Yang, H. Xu and R. Wu, *Chem. Eng. J.*, , DOI:10.1016/j.cej.2020.124926.
- 12 X. Liu, Y. Yang and S. Guan, *Chem. Phys. Lett.*, 2017, **675**, 11–14.
- 13 X. Zhao, J. Meng, Z. Yan, F. Cheng and J. Chen, *Chinese Chem. Lett.*, 2019, **30**, 319–323.
- 14 Y. Zhang, H. Guo, P. Yuan, K. Pang, B. Cao, X. Wu, L. Zheng and R. Song, *J. Power Sources*, 2019, **442**, 227252.
- 15 S. Zhang, G. She, S. Li, F. Qu, L. Mu and W. Shi, *Catal. Commun.*, 2019, **129**, 105725.