

Electronic Supplementary Information for:

Highly active two dimensional $\alpha\text{-MoO}_{3-x}$ for electrocatalytic hydrogen evolution reaction

R. S. Datta, F. Haque, M. Mohiuddin, B. J. Carey, N. Syed, A. Zavabeti, B. Zhang, H. Khan, K. J. Berean, J. Z. Ou, N. Mahmood, T. Daeneke, K. Kalantar-zadeh[†]

School of Engineering, RMIT University, Melbourne, VIC 3001, Australia

[†] Correspondence to kourosh.kalantar@rmit.edu.au

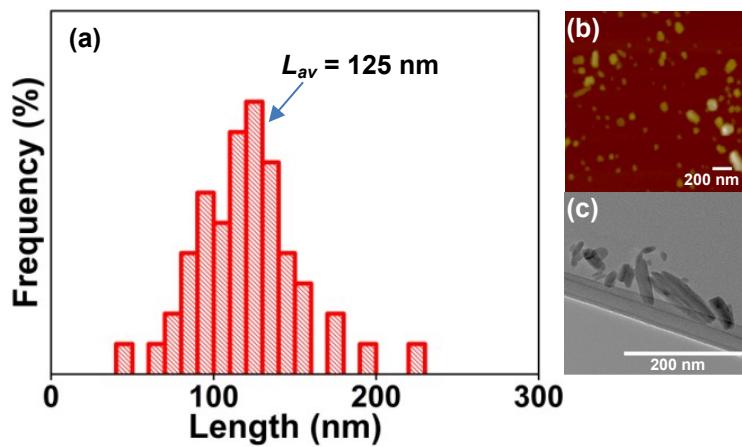


Fig. S1 (a) Frequency histogram of the observed lateral sizes of 2D MoO_{3-x} nanosheets using AFM, (b) large area AFM image of 2D MoO_{3-x} nanosheets, and (c) large area TEM image showing the 2D MoO_{3-x} nanosheets.

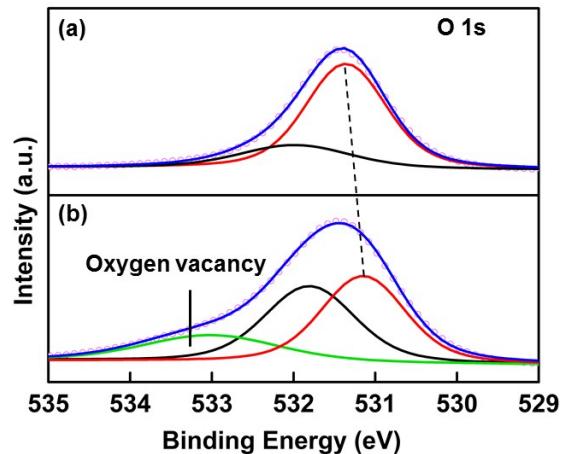


Fig. S2 O 1s XPS spectra of (a) bulk $\alpha\text{-MoO}_3$ and (b) 2D $\alpha\text{-MoO}_{3-x}$.

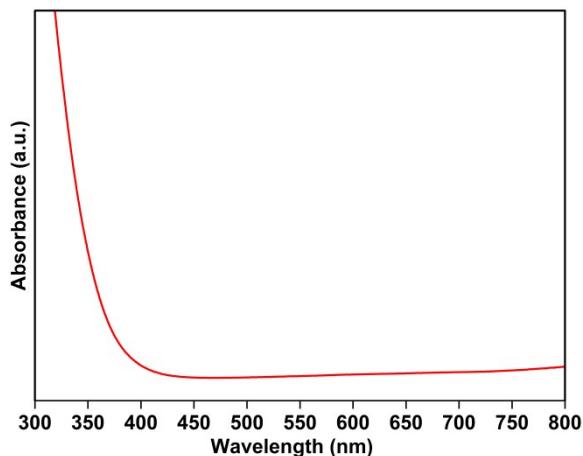


Fig. S3 UV-Vis spectrum of 2D $\alpha\text{-MoO}_{3-x}$ suspension.

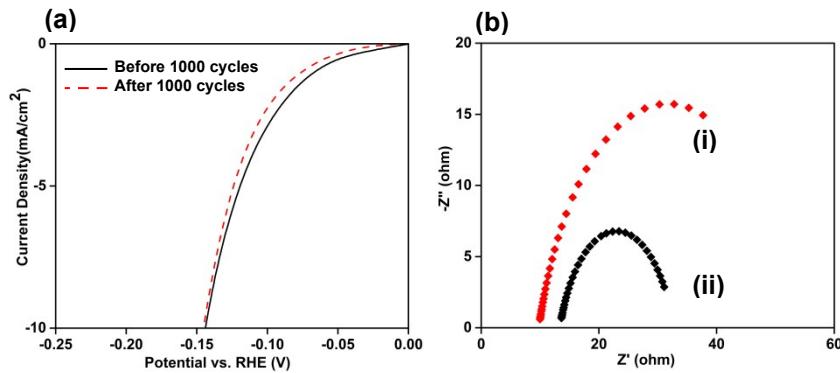


Fig. S4 (a) Linear sweep voltammogram recorded for 2D α -MoO_{3-x} before and after 1000 cycles of cyclic voltammetry and (b) Fitted Nyquist plot of (i) bulk α -MoO₃ and (ii) 2D α -MoO_{3-x} at 0.17V vs. RHE.

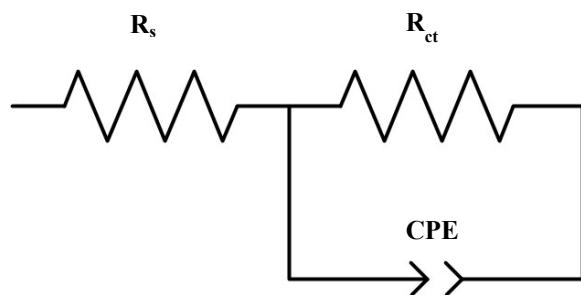


Fig. S5 Equivalent circuit applied to obtain charge transfer resistance of the catalysts in 0.1 M KOH.

Here,

R_s : resistance of the electrolyte

R_{ct} : charge transfer resistance

CPE: constant phase element

Table S1. Impedance components for HER determined by fitting the experimental EIS data using the equivalent circuit shown in **Fig. S4**

Material	$R_s(\Omega)$	$R_{ct}(\Omega/\text{cm}^2)$	CPE(mF/cm ²)
2D α -MoO _{3-x}	13.3	19.3	0.78
Bulk α -MoO ₃	9.7	43.7	0.79

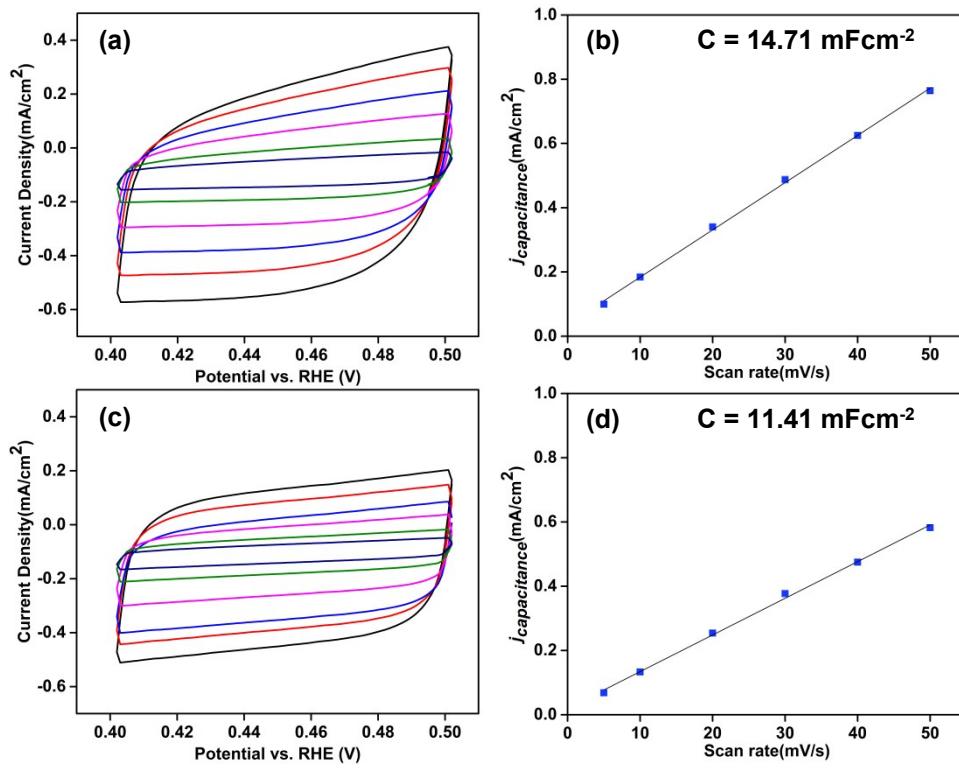


Fig. S6 (a,b) Determination of electrochemical double-layer capacitance of 2D α -MoO_{3-x} nanosheets over a range of scan rates at 0.45 V vs RHE in 0.1M KOH and (c,d) determination of electrochemical double-layer capacitance of bulk α -MoO₃ over a range of scan rates at 0.45 V vs RHE in 0.1M KOH.

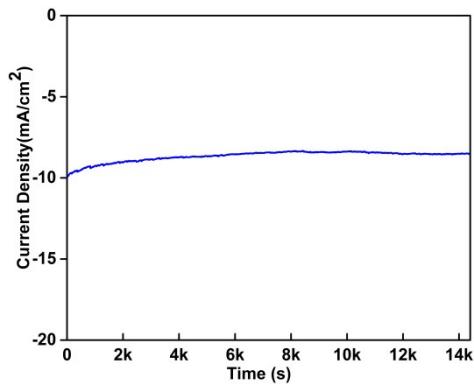


Fig. S7 Time-dependent current density of 2D α -MoO_{3-x} nanosheets during HER with 14.4k seconds at fixed overpotential of 0.14 V vs RHE.

Table S2. Comparison of the overpotentials and corresponding Tafel slopes of molybdenum oxides, their compounds and heterostructures as well as selected reports on two dimensional molybdenum sulphides.

Material	Tafel slope (mV dec ⁻¹)	Overpotential (mV)	Reference
Polycrystalline Pt		21	1
Mesoporous MoO_{3-x}	56	148	2
Core–shell MoO₃–MoS₂ nanowires	60	250	3
MoO₂/rGO composite	68	310	4
P doped MoO_{3-x}	42	166	5
Metallic 1T MoS₂ sheets	43	187	6
Defect-rich MoS₂ sheets	50	~195	7
Amorphous MoS₂	60	~200	8
2D MoO_{3-x}	58	142	This work

References

1. J. D. Benck, T. R. Hellstern, J. Kibsgaard, P. Chakthranont and T. F. Jaramillo, *ACS Catal.*, 2014, **4**, 3957-3971.
2. Z. Luo, R. Miao, T. D. Huan, I. M. Mosa, A. S. Poyraz, W. Zhong, J. E. Cloud, D. A. Kriz, S. Thanneeru, J. He, Y. Zhang, R. Ramprasad and S. L. Suib, *Adv. Energy Mater.*, 2016, **6**, 1600528.
3. Z. Chen, D. Cummins, B. N. Reinecke, E. Clark, M. K. Sunkara and T. F. Jaramillo, *Nano Lett.*, 2011, **11**, 4168-4175.
4. L. Wu, X. Wang, Y. Sun, Y. Liu and J. Li, *Nanoscale*, 2015, **7**, 7040-7044.
5. L. Li, T. Zhang, J. Yan, X. Cai and S. Liu, *Small*, 2017, **13**, 1700441.
6. M. A. Lukowski, A. S. Daniel, F. Meng, A. Forticaux, L. Li and S. Jin, *J. Am. Chem. Soc.*, 2013, **135**, 10274-10277.
7. J. Xie, H. Zhang, S. Li, R. Wang, X. Sun, M. Zhou, J. Zhou, X. W. Lou and Y. Xie, *Adv. Mater.*, 2013, **25**, 5807-5813.
8. J. D. Benck, Z. Chen, L. Y. Kuritzky, A. J. Forman and T. F. Jaramillo, *ACS Catal.*, 2012, **2**, 1916-1923.