

Electronic Supplementary Information (ESI)

Metal organic framework-guided growth of Mo₂C embedded in mesoporous carbon as high-performance and stable electrocatalyst for hydrogen evolution reaction

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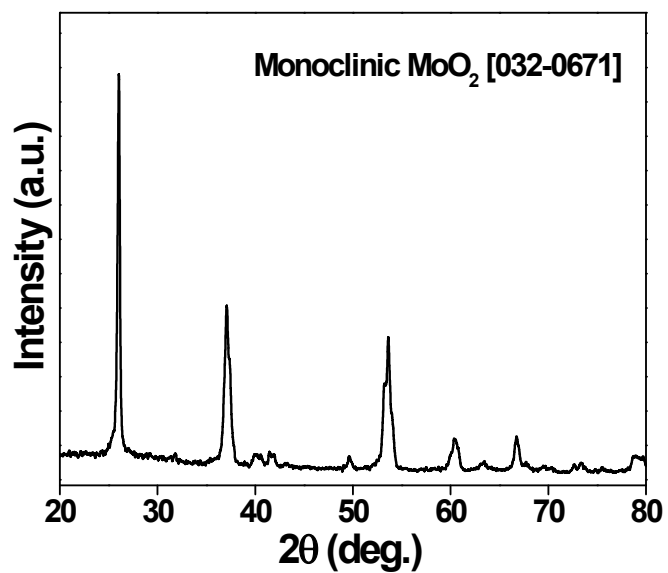


Figure S1. XRD spectra of MoO₂ obtained at 800 °C annealed under N₂ gas.

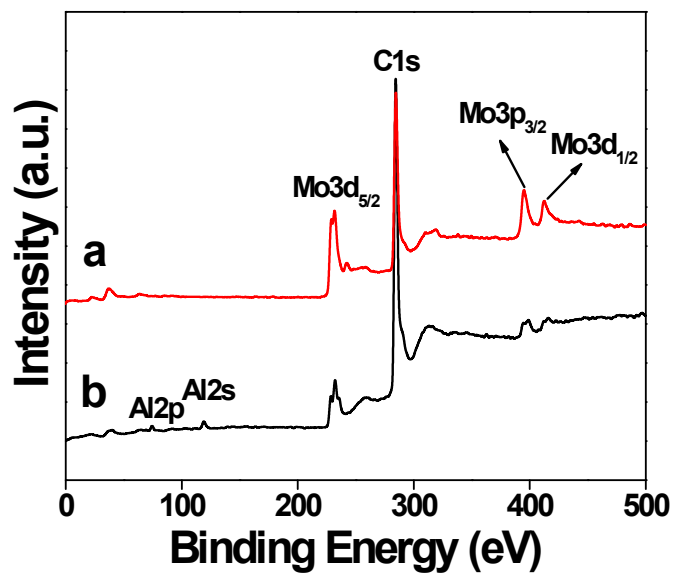


Figure S2. XPS survey spectra of Mo₂C/C before (a) and after Al removal (b).

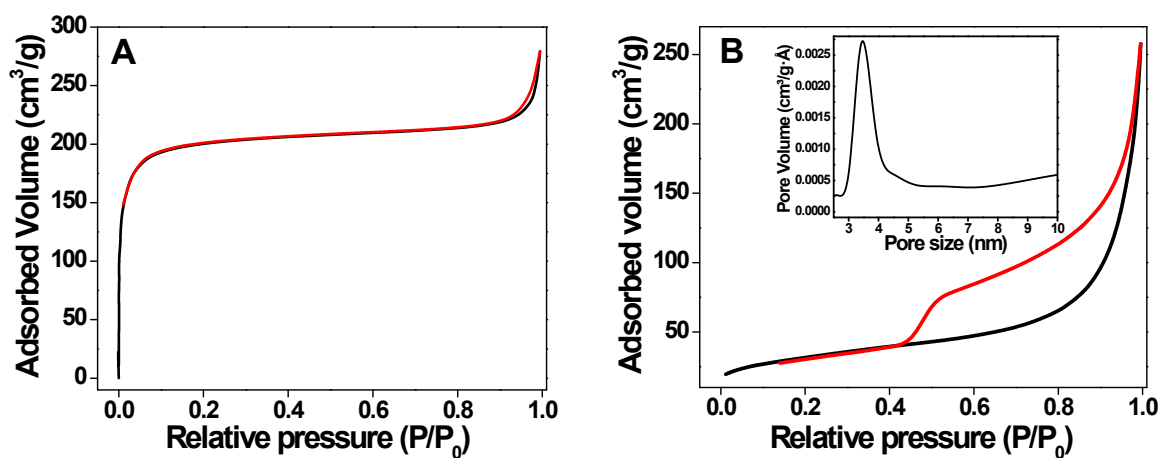


Figure S3. BET isotherms of (A) MIL-53(Al) and (B) Mo₂C/C nanocomposite together with pore size distribution (Fig. B inset).

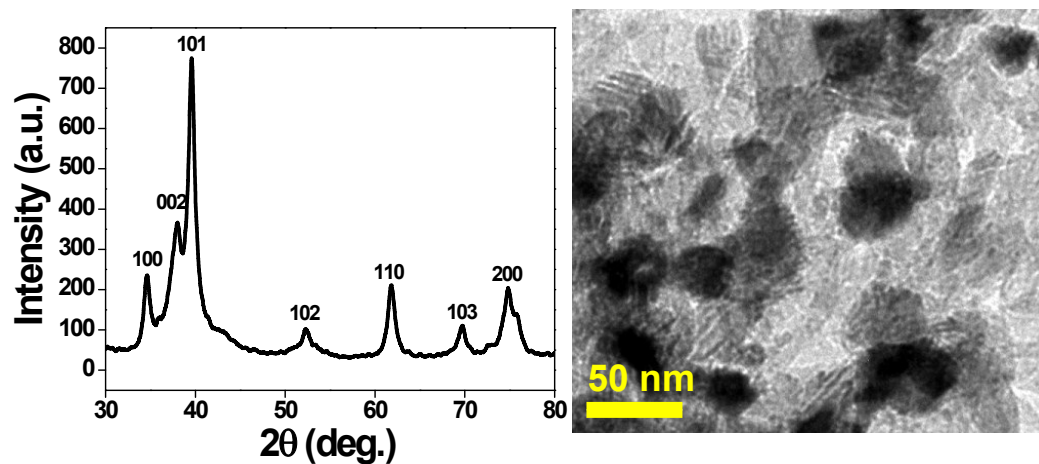


Figure S4. XRD and TEM of Mo₂C/XC.

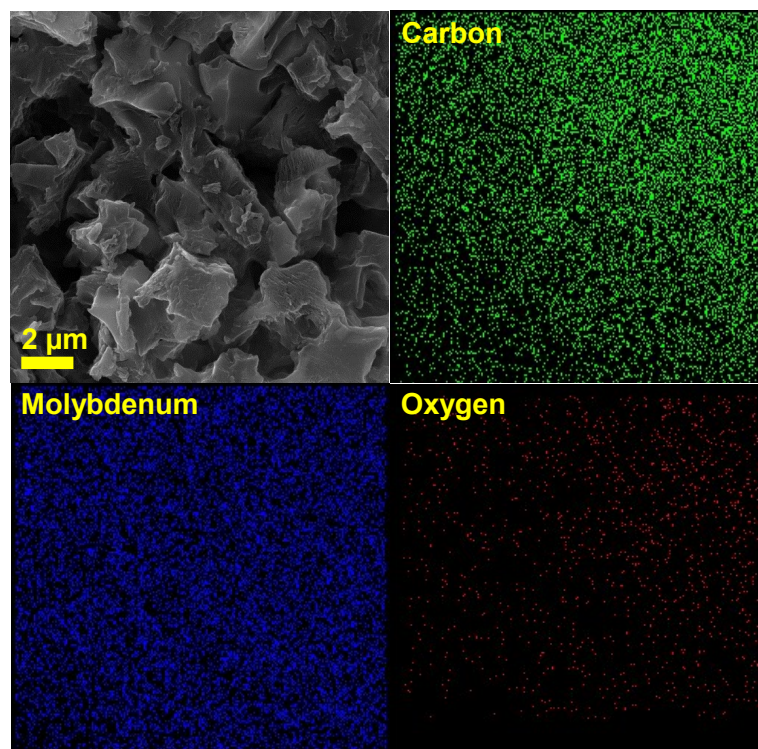


Figure S5. SEM and elemental mapping of carbon, molybdenum and oxygen present in $\text{Mo}_2\text{C}/\text{C}$.

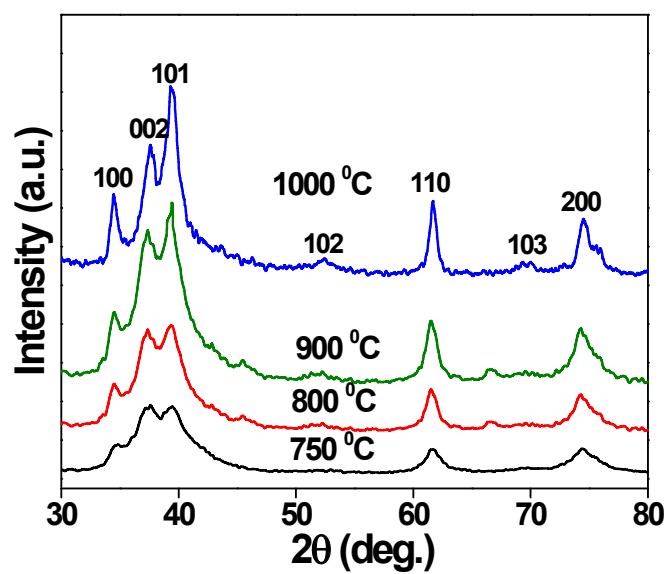


Figure S6. XRD spectra of $\text{Mo}_2\text{C}/\text{C}$ carburized at different temperature.

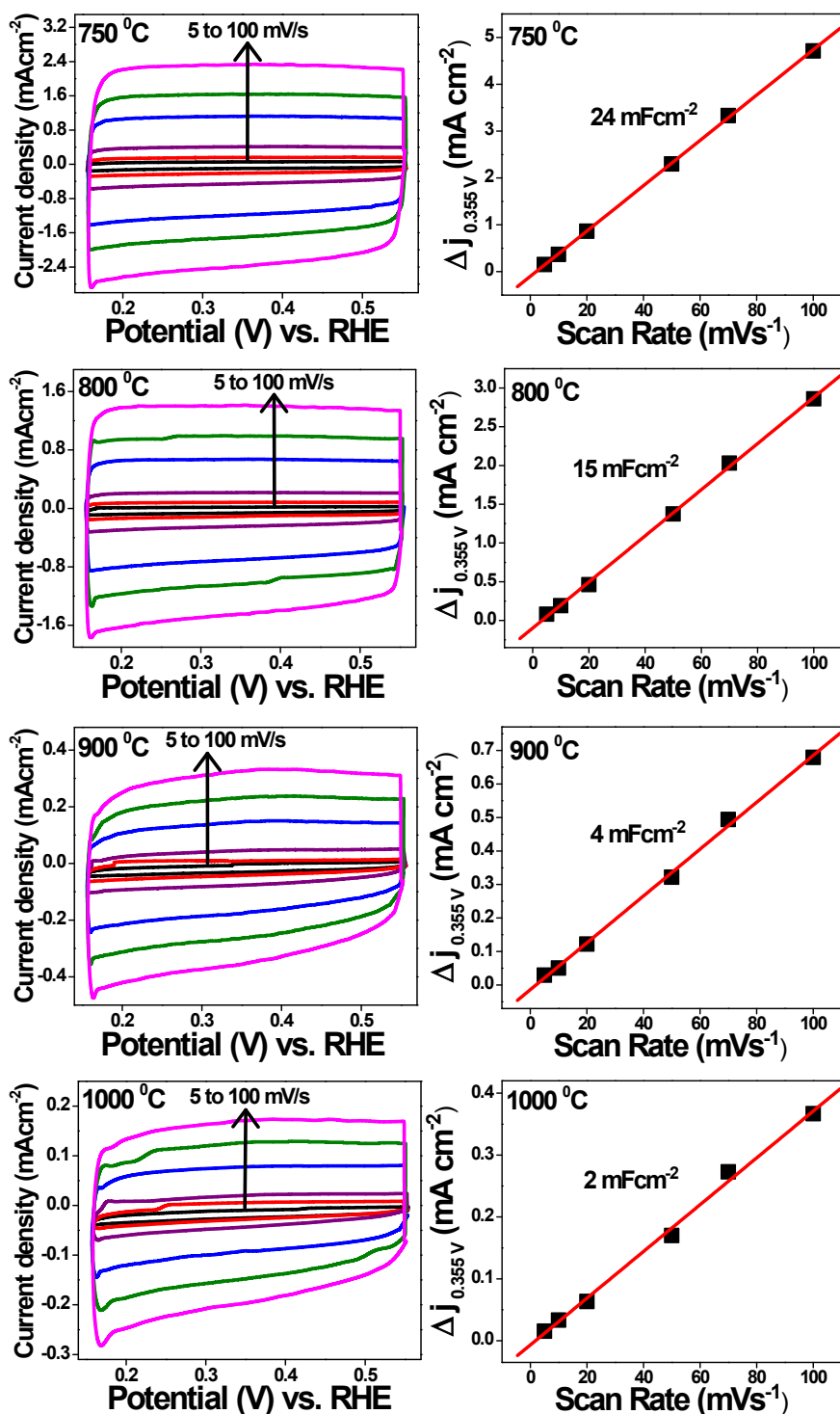


Figure S7. Effect of annealing temperature on cyclic voltammograms (CVs) of Mo₂C/C recorded at different scan rates from 5 to 100 mVs⁻¹, and their corresponding plots of the current density at 0.355 V_{RHE} vs. scan rate. CVs were recorded in non-faradic region. The linear slopes are equivalent to twice of the electrochemical double layer capacitance (C_{dl}).

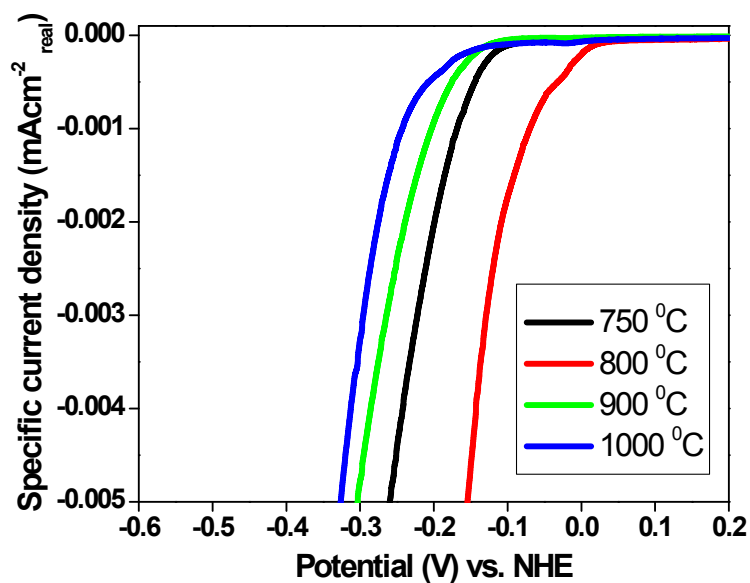


Figure S8. Potentiodynamic curves showing the effect of temperature on specific current density calculated with real surface area.

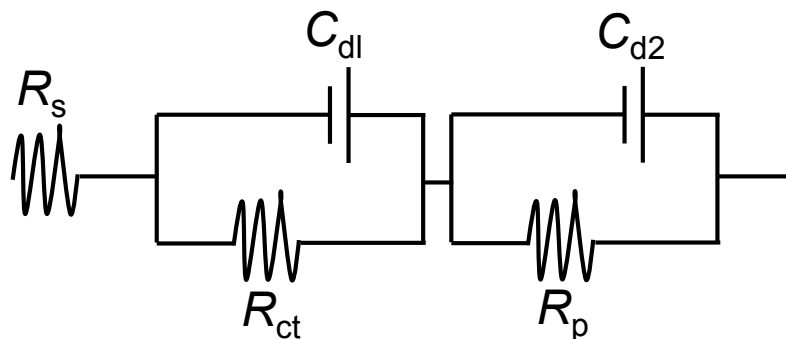


Figure S9. Two time constant electrical equivalent circuit model utilized to fit the electrochemical impedance (EIS) results of hydrogen evolution reaction. R_s – series resistance, C_{dl} and C_{d2} are double layer capacitance, R_{ct} – charge transfer resistance for HER, R_p – resistance related to the surface porosity.

Table S1. Comparison of electrocatalysts (Mo₂C) for HER.

Catalysts	Electrolyte	Overpotential at 10 mA cm ⁻² (mV)	Tafel slope (mV dec ⁻¹)	Catalyst loading (mg cm ⁻²)
α -Mo ₂ C ¹	0.5 M H ₂ SO ₄	198	56	0.102
α -Mo ₂ C ¹	1 M KOH	176	58	0.102
Mo ₂ C/CNT ²	0.1 M HClO ₄	250	251	8.2
Mo ₂ C/CXG ²	0.1 M HClO ₄	170	264	6.3
Mo ₂ C/CNT ³	0.5 M H ₂ SO ₄	190	63	0.65-0.67
Mo ₂ C/CNT-GR ³	0.5 M H ₂ SO ₄	130	58	0.65-0.67
Mo ₂ C/GR ⁴	0.5 M H ₂ SO ₄	242	82	0.65-0.67
Mo ₂ C/CNT ⁴	0.1 M HClO ₄	152	55.2	2
Bulk Mo ₂ C ⁴	0.1 M HClO ₄	~300	87.6	2
3DHP-Mo ₂ C ⁵	0.5 M H ₂ SO ₄	97	60	0.28
Mo ₂ C/NCNTs ⁶	0.5 M H ₂ SO ₄	147	71	3
Mo ₂ C/CNTs ⁶	0.5 M H ₂ SO ₄	179	65	3
Mo ₂ C/RGO ⁷	0.5 M H ₂ SO ₄	130	57.3	0.285
MoC _{x-2} ⁸	0.5 M H ₂ SO ₄	160	93	0.354
Mo ₂ C nanowires ⁹	0.5 M H ₂ SO ₄	200	52	0.21
Mo ₂ C/CC ¹⁰	0.5 M H ₂ SO ₄	140	124	1.5
Mo ₂ C ¹¹	0.1 M HClO ₄	>250	120	0.28
Mo ₂ C ¹²	1 M KOH	176	58	0.102
Mo ₂ C-carbon ¹³	0.05 M H ₂ SO ₄	>270	-	0.25
Mo ₂ C ¹⁴	1 M H ₂ SO ₄	~210	56	1.4
Mo ₂ C ¹⁴	1 M KOH	~190	54	0.8
Mo ₂ C/C ^a	1 M KOH	165	66.41	1.0

η : overpotential, GR: graphene, CNTs: carbon nanotubes, a = in this study

References

- 1 L. Ma, L. R. L. Ting, V. Molinari, C. Giordano, B. S. Yeo, *J. Mater. Chem. A*, 2015, **3**, 8361–8368.
- 2 B. Šljukić, M. Vujković, L. Amaral, D. M. Santos, R. P. Rocha, C. A. Sequeira, J. L. Figueiredo, *J. Mater. Chem. A*, 2015, **3**, 15505-12.
- 3 D. H. Youn, S. Han, J. Y. Kim, J. Y. Kim, H. Park, S. Choi and J. S. Lee, *ACS Nano*, 2014, **8**, 5164–5173.
- 4 W. F. Chen, C. H. Wang, K. Sasaki, N. Marinkovic, W. Xu, J. T. Muckerman, Y. Zhu, R. R. Adzic, *Energy Environ. Sci.*, 2013, **6**, 943–951.
- 5 H. Ang, H. Wang, B. Li, Y. Zong, X. Wang, and Q. Yan, *Small*, 2016, **12**, 2859–2865.
- 6 K. Zhang, Y. Zhao, D. Fu, Y. Chen, *J. Mater. Chem. A*, 2015, **3**, 5783–5788.
- 7 L. F. Pan, Y. H. Li, S. Yang, P. F. Liu, M. Q. Yua, H. G. Yang, *Chem. Commun.*, 2014, **50**, 13135-13137.
- 8 X. Yang, X. Feng, H. Tan, H. Zang, X. Wang, Y. Wang, E. Wang, Y. Li, *J. Mater. Chem. A*, 2016, **4**, 3947–3954.
- 9 L. Liao, S. Wang, J. Xiao, X. Bian, Y. Zhang, M. D. Scanlon, X. Hu, Y. Tang, B. Liu, H. H. Girault, *Energy Environ. Sci.*, 2014, **7**, 387-392.
- 10 M. Fan, H. Chen, Y. Wu, L. L. Feng, Y. Liu, G. D. Li, X. Zou, *J. Mater. Chem. A*, 2015, **3**, 16320-6.
- 11 C. Wan, Y. N. Regmi and B. M. Leonard, *Angew. Chem., Int. Ed.*, 2014, **53**, 6407–6410.
- 12 L. Ma, L. R. Ting, V. Molinari, C. Giordano, B. S. Yeo, *J. Mater. Chem. A*, 2015, **3**, 8361–8368.
- 13 N. S. Alhajri, D. H. Anjum and K. Takanabe, *J. Mater. Chem. A*, 2014, **2**, 10548–10556.
- 14 H. Vrubel and X. L. Hu, *Angew. Chem., Int. Ed.*, 2012, **51**, 12703–12706.