Electronic Supplementary Information for

In situ embedding Mo₂C/MoO_{3-x} nanoparticles within a carbonized wood membrane as a self-supported pH-compatible cathode for efficient electrocatalytic H₂ evolution

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Fig. S1 (a) The cyclic voltammograms (CV) of Pt wire working electrode in the high purity hydrogen saturated 0.5 M H_2SO_4 and (b) 1 M KOH electrolyte solution. The CV scans were run at a scan rate of 5 mV s⁻¹, and the average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode.



Fig.S2 XRD patterns of the NW, MoO_x@NW-HT, MoO_x@NW-LT, and MCWM-2 electrode. The marks "I", "II", and "III" in the XRD spectrum of the NW slice indicate the diffraction peaks of (002) planes (I) and amorphous phase (II) of the cellulose and crystalline hemicellulose (III), respectively.



Fig. S3 (a) XPS survey spectra. High-resolution (b) C 1s, (c) O 1s, and (d) N 1s XPS spectra of the MCWM-1, MCWM-2 and MCWM-3 electrodes.

Sample	Loading amount of Mo (mg cm ⁻²)
MCWM-1	0.5933
MCWM-2	0.5965
MCWM-3	0.5980

Table S1 ICP-OES analysis for the MCWM electrodes.

Table S2 The summary of content for different Mo species in different electrodes.

Sample	Mo ₂ C —	MoO _{3-x}			
		Mo^{5+}	Mo ⁶⁺	1V102C/1V103-x	
MCWM-1	15.03%	4.97%	80.00%	0.186	
MCWM-2	10.40%	5.21%	84.39%	0.116	
MCWM-3	25.93%	5.99%	68.08%	0.350	
MCWM-2 after					
HER stability test	27.24%	5.11%	67.65%	0.374	
in 0.5 M H ₂ SO ₄					
MCWM-2 after					
HER stability test	23.24%	5.24%	71.52%	0.303	
in 1M KOH					



Fig. S4 (a, b) Top-view SEM images of the CWM electrode and (c) the corresponding EDS element mapping images. (d, e) Side-view SEM images of the CWM electrode and (f) the corresponding EDS element mapping images.

	solution.				
Sample	Overpotential (mV)	Tafel slop	Self-	Reference	
	at 10 mA cm ⁻²	(mV dec ⁻¹)	supported		
MCWM-2	186	134	Yes	This work	
MoP NA/CC	124	58	Yes	1	
Mo ₂ C@NC	60	-	No	2	
MoC@GC	124	43	No	3	
N,P-Doped Mo ₂ C@C	141	71	No	4	
P-MoO _{3-x}	166	42	No	5	
Mesoporous MoO _{3-x}	179	72	No	6	
a-Mo ₂ C	198	56	No	7	
Mo ₂ C/GCSs	200	62.5	No	8	
Mo ₂ C	208	56	No	9	
Mo ₂ N/CNT	218	133	No	10	
MoP	246	60	No	11	
MoC ₂ NWAs/CFP	190	68	Yes	12	

Table S3. HER activities of various non-noble metal electrocatalysts in 0.5 M H₂SO₄



Fig. S5 (a) Digital photo of the MCWM-2 electrode after a 12 h of HER stability test in 0.5 M H₂SO₄. (b) Top-view and (c) side-view SEM images of the MCWM-2 electrode and the corresponding EDX elemental maps. (d) XRD pattern and (e) Mo3d XPS spectrum of the used MCWM-2 electrode after a 12 h of HER stability test in 0.5 M H₂SO₄.

	solution.				
Sample	Overpotential (mV)	Tafel slop	Self-	Deference	
	at 10 mA cm ⁻²	$(mV dec^{-1})$	supported	Reference	
MCWM-2	275.3	134	Yes	This work	
MoC ₂ NWAs/CFP	170	72	Yes	12	
γ- Mo ₂ N@NC	85	54	No	13	
Mo ₂ C/carbon	100	65	No	14	
Microflowers	100				
Mo ₂ C@NC	124	60	No	15	
MoC _x	151	59	No	16	
MoC@NC	170	51	No	17	
Mo ₂ C	190	54	No	9	
P-MoO _{3-x}	233	53	No	5	
Core-shell MoO ₃ -MoS ₂ nanowires	250	60	No	18	
Mo ₂ C	290	216	No	19	
MoO ₂ /rGO	310	68	No	20	
Mo ₂ C/NGA	365	-	Yes	21	

Table S4 HER activities of various non-noble metal electrocatalysts in 1.0 M KOH



Fig. S6 (a) Digital photo of the MCWM-2 electrode after a 12 h of HER stability test in 1.0 M KOH. (b) Top-view and (c) side-view SEM images of the MCWM-2 electrode and the corresponding EDX elemental maps. (d) XRD pattern and (e) Mo3d XPS spectrum of the used MCWM-2 electrode after a 12 h of HER stability test in 1.0 M KOH.

References

- 1. Z. Pu, S. Wei, Z, Chen, S, Mu, Appl. Catal. B: Environ. 2016, 196, 193-198.
- 2. R. Ma, Y. Zhou, Y. Chen, P. Li, Q. Liu, J. Wang, Angew. Chem. Int. Edit. 2015, 54, 14723-14727.
- 3. Z. Shi, Y. Wang, H. Lin, H. Zhang, M, Shen, S. Xie, Y. Zhang, Q. Gao, Y. Tang, J. Mater. Chem. A 2016, 4, 6006-6013.
- 4. Y.-Y. Chen, Y. Zhang, W.-J. Jiang, X. Zhang, Z. Dai; L.-J. Wan, J.-S. Hu, ACS Nano 2016, 10, 8851-8860.
- 5. L. Li, T. Zhang, J. Yan, X. Cai, S. Liu, Small 2017, 13, 1700441.
- 6. J. Han, X. Ji, X. Ren, G. Cui, L. Li; F. Xie, J. Mater. Chem. A 2018, 6, 12974-12977.
- 7. L. Ma; R. L. Ting, V. Molinari, C. Giordano, B. S. Yeo, J. Mater. Chem. A 2015, 3, 8361-8368.
- 8. W. Cui, N. Cheng, Q. Liu, C. Ge, A. M. Asiri, X. Sun, ACS Catal. 2014, 4, 2658-2661.
- 9. H. Vrubel, X. Hu, Angew. Chem. Int. Edit. 2012, 51, 12703-12706.
- 10. M. Meng, H. Yan, Y. Jiao, A. Wu, X. Zhang, R. Wang, C. Tian, RSC Adv. 2016, 6, 29303-29307.
- 11. X. Chen, D. Wang, Z. Wang, P. Zhou, Z. Wu, F. Jiang, Chem. Commun. 2014, 50, 11683-11685.
- 12. X. Zhang, F. Zhou, W. Pan, Y. Liang and R. Wang, Adv. Funct. Mater., 2018, 28, 1804600.
- 13. Z. Lv, M. Tahir, X. Lang, G. Yuan, L. Pan, X. Zhang, J.-J. Zou, J. Mater. Chem. **R8**

A 2017, **5**, 20932-20937.

- Y. Huang, Q. Gong, X. Song, K. Feng, K. Nie, F. Zhao, Y. Wang, M. Zeng, J. Zhong, Y. Li, ACS Nano 2016, 10, 11337-11343.
- Y. Liu, G. Yu, G.-D. Li, Y. Sun, T. Asefa, W. Chen, X. Zou, Angew. Chem. Int. Edit. 2015, 54, 10752-10757.
- H.-W. Liang, S. Brüller, R. Dong, J. Zhang, X. Feng, K. Müllen, *Nat. Commun.* 2015, 6, 7992.
- Z. Cheng, J. Gao, Q. Fu, C. Li, X. Wang, Y. Xiao, Y. Zhao, Z. Zhang, L. Qu, ACS Appl. Mater. Inter. 2017, 9, 24608-24615.
- Z. Chen, D. Cummins, B. N. Reinecke, E. Clark, M. K. Sunkara, T. F. Jaramillo, Nano Lett. 2011, 11, 4168-4175.
- J. Wang, H. Xia, Z. Peng, C. Lv, L. Jin, Y. Zhao, Z. Huang, C. Zhang. ChemSusChem 2016, 9, 855-862.
- 20. L. Wu, X. Wang, Y. Sun, Y. Liu, J. Li, Nanoscale 2015, 7, 7040-7044.
- 21. Y. Zhou, J. Niu, G. Zhang, M. Yu and F. Yang, Environ. Res., 2020, 184, 109283