Supporting Information

Carbon impurities-free, novel Mn, N co-doped porous Mo₂C

nanorods for efficient and stable hydrogen evolution reaction

Yajun Zhou,^{#[a]} Jieyu Xu,^{#[a]} Cheng Lian,^[b] Lin Ge,^[c] Lingxia Zhang,^[d] Liang Li, ^[a] Yunheng Li, ^[a] Min Wang, ^[a, d] Honglai Liu,^[b] and Yongsheng Li*^[a]

[a] Lab of Low-Dimensional Materials Chemistry, Key Laboratory for Ultrafine Materials of Ministry of Education, Shanghai Engineering Research Center of Hierarchical Nanomaterials, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China;

[b] State Key Laboratory of Chemical Engineering, Shanghai Engineering Research Center of Hierarchical Nanomaterials, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China;

[c] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, Engineering, China;

[d] State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China.

E-mail: ysli@ecust.edu.cn



Fig. S1 XRD pattern of Mn, N-Mo₂C-0.3.



Fig. S2 SEM images of Mn, N-Mo₂C-0 (a-b) and Mn, N-Mo₂C-0.01 (c-d).

Sample	Mn wt%		
Mn, N-Mo ₂ C-0	0		
Mn, N-Mo ₂ C-0.001	0		
Mn, N-Mo ₂ C-0.005	0.38		
Mn, N-Mo ₂ C-0.01	0.77		
Mn, N-Mo ₂ C-0.05	3.3		

Tab. S1 Mn contents of Mn, N-doped Mo₂C electrocatalysts measured by ICP-OES.



Fig. S3 (a) XPS survey spectrum, (b) C 1s, and (c) Mo 3d high-resolution XPS spectra of Mn, N-Mo₂C-0.



Fig. S4 (a) Mn 2p high-resolution and (b) XPS survey spectra of Mn, N-Mo₂C-0.01.



Fig. S5 Capacitive current at 0.15 V as a function of scan rate for Mn, N-doped Mo₂C electrocatalysts ($\Delta j_0 = j_a$ - j_c) in the potential range of 0-0.3 V, where no Faradaic process occured.



Fig. S6 (a) XRD patterns of Mn, N-Mo₂C-0.01 before and after HER test (1000 CV cycles). (b)
SEM image, (c, d) TEM images for Mn, N-Mo₂C-0.01 after 1000 CV cycles. The inset in Fig, S6d is the HRTEM image of Mn, N-Mo₂C-0.01 after 1000 CV cycles.

Tab. S2 Comparison of the electrocatalytic activity of Mn, N-Mo ₂ C-0.01 and other related	d
electrocatalysts reported for HER in acid solution.	

	Loading	Current	Overpotential at	Tafel			
Catalyst	density	density j	the corresponding	slope	Reference		
	$(mg cm^{-2})$	$(mA cm^{-2})$	j (mV)	(mV dec ⁻¹)			
Mn, N-Mo ₂ C-0.01	~0.55	10	163	66	This work		
Mo ₂ N-Mo ₂ C/	Mo ₂ N-Mo ₂ C/	0.227 10	157	55	Adv. Mater. 2018, 30,		
HGr-3	~0.337	10	157		1704156		
M. C/CNT CD	~0.65 10 1	10	120	50	ACS Nano		
M0 ₂ C/CN1-GK		130	58	2014, 8, 5164			
Mo-Mo ₂ C-0.077	~0.38	10	150	55	J. Mater. Chem. A,		
		10			2018, 6, 10028		
Mo ₂ C-GNR	/	10	152	65	ACS Nano		
					2017, 11, 384		
Co-Mo ₂ C-0.020	0.14	10	140	39	Adv. Funct. Mater.		
			140		2016, 26, 5590		
C-NCOM-C	0.92	10	142	142	10 142	(0)	Nano Energy
Co-INC@MO2C	~0.85	10	143	60	57, (2019), 746		
Mo ₂ C@NC	10	24	22.7	Adv. Funct. Mater.			
nanomesh	0.5	10 56	10	10 36 33.7	33.7	2018, 28, 1705967	
uf-Mo ₂ C/CF-2	0.25	10	184	71	Small Methods		
					2018, 1700396		
Mo ₂ C/C (2:2)	0.28	10	180	71	ACS Appl. Mater.		
		10			Inter., 2017, 9, 41314		