Supporting Information

Ultra-small Mo_2C Nanodots Encapsulated in Nitrogen Doped Porous Carbon for pH-universal Hydrogen Evolution: Insights into the Synergetic Enhancement by Nitrogen Doping and Structure Defects

Weiwei Han[1‡], Lulu Chen[2‡], Biao Ma[1], Jun Wang[1], Weiyu Song[2*], Xiaobin Fan[1], Yang Li[1], Fengbao Zhang[1], and Wenchao Peng[1*]

[1]School of Chemical Engineering and Technology, Tianjin University, Tianjin 300050, China.

(*Corresponding author: e-mail: wenchao.peng@tju.edu.cn)

[2]State Key Laboratory of Heavy Oil Processing, College of Science, China University of Petroleum-Beijing, Beijing 102249, China

(*Corresponding author: e-mail: songwy@cup.edu.cn)

‡ The authors contribute equal to this manuscript.

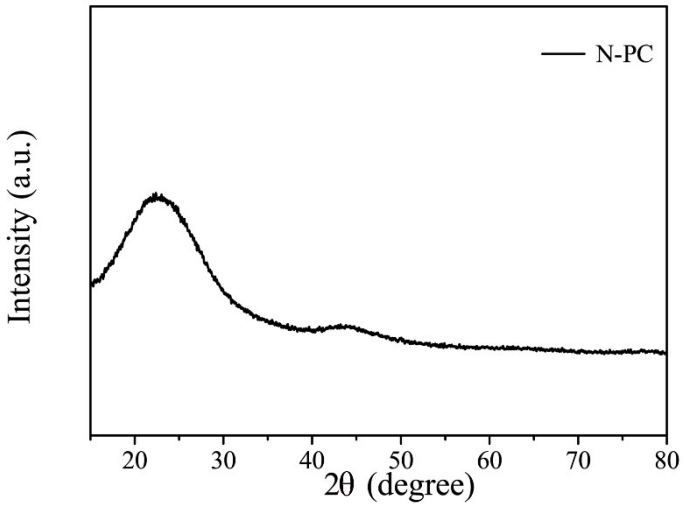

Figure S1. XRD pattern of N-PC.

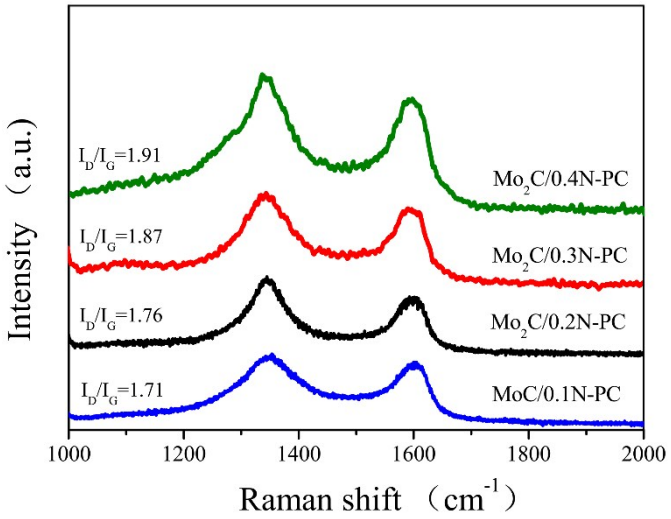

Figure S2. Raman spectra of Mo_xC/yN-PC with different nitrogen doping content.

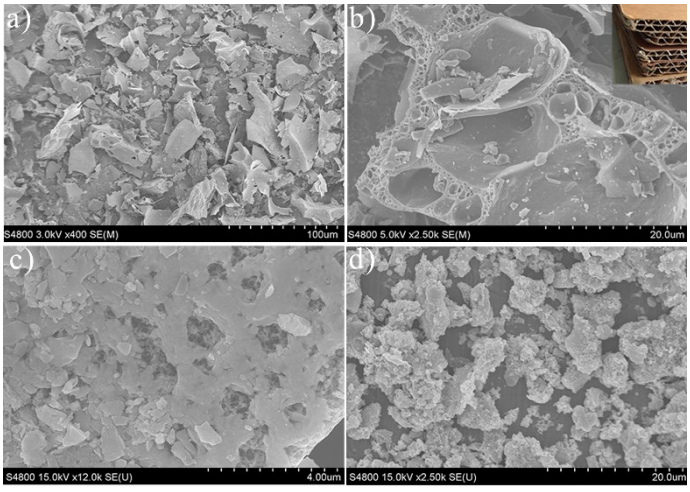

Figure S3. SEM images of a), b) N-PC; c) MoC/C; d) Mo_2C/N-PC.

Table S1. Elemental compositions of Mo_xC/yN-PC samples by STEM-EDS.

	Mo (at%)	C (at%)	N (at%)	O (at%)
MoC/0.1N-PC	21.34	65.36	1.8	11.5
Mo_2C/0.2N-PC	34.11	54.1	2.69	9.1
Mo_2C/0.3N-PC	29.1	50.91	2.89	17.1
Mo_2C/0.4N-PC	32.23	48.26	3.01	16.5

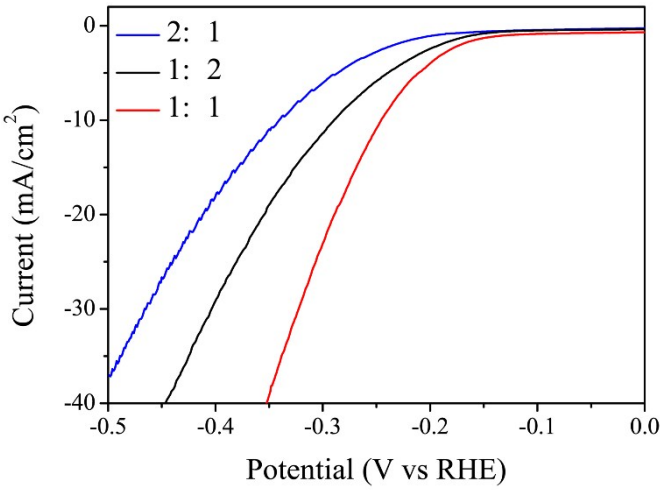

Figure S4. Comparison of HER activity of MoC/C with different precursor mass ratios (starch: ammonium molybdate) in 0.5 M H_2SO_4.

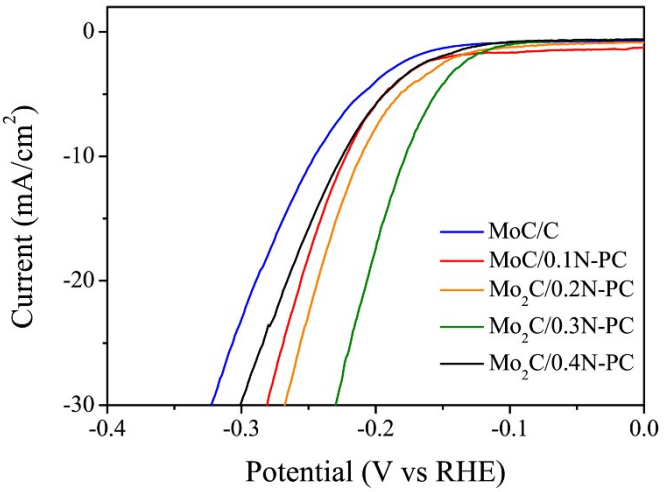

Figure S5. Comparison of HER activity of Mo_xC/yN-PC with different nitrogen doping content in 0.5 M H_2SO_4.

Table S2. Summary of the Hydrogen Evolution Reaction catalytic characteristics (overpotential at 10 mA·cm^{-2} and Tafel slope) of N-PC, com Mo_2C, MoC/C, Mo_2C/N-PC and Pt/C (20 wt%) catalysts.

Catalysts	pH	Tafel slope (mV· dec^{-1})	Overpotential (mV vs. RHE) at 10 mA·cm^{-2}
N-PC	0	194.5	396
	7	522.7	—
	14	331.0	446
com Mo_2C	0	99.5	293
	7	107.3	363
	14	100.8	231
MoC/C	0	101.7	246
	7	118.8	319
	14	114.1	205
Mo_2C/N-PC	0	72.3	178
	7	140.8	224
	14	94.5	100
Pt/C (20 wt%)	0	32.1	34
	7	58.5	56
	14	43.5	21

Table S3. Comparison of HER activities with other recently reported Mo_2C based catalysts.

Catalysts	Overpotential (mV vs. RHE) at 10 mA·cm^{-2}	Tafel Slope (mV· dec^{-1})	Electrolyte	Reference
MoC–Mo_2C	126	43	0.5 M H_2SO_4	1
	120	42	1 M KOH	
Mo_2C/C	180	71	0.5 M H_2SO_4	2
	125	72	1 M KOH	
MoC_x/ porous N, S-doped graphene	135	62	0.5 M H_2SO_4	3
	165	105	0.2 M PBS	
	150	99	1 M NaOH	
np-Mo_2C	229	100.7	0.5 M H_2SO_4	4
Mo_2C/ 3D N-doped carbon microflower	144	55	0.5 M H_2SO_4	5
	100	65	1 M KOH	
Mo_2C@ B,N-doped C	100	62	1 M KOH	6
Mo_2C@NC	150	97		
Mo_2C@C	240	83	0.5 M H_2SO_4	7
	189	70	1 M KOH	
Mo_2C/N-PC	178	72.3	0.5 M H_2SO_4	this work
	224	140.8	1 M PBS	
	100	94.5	1 M KOH	

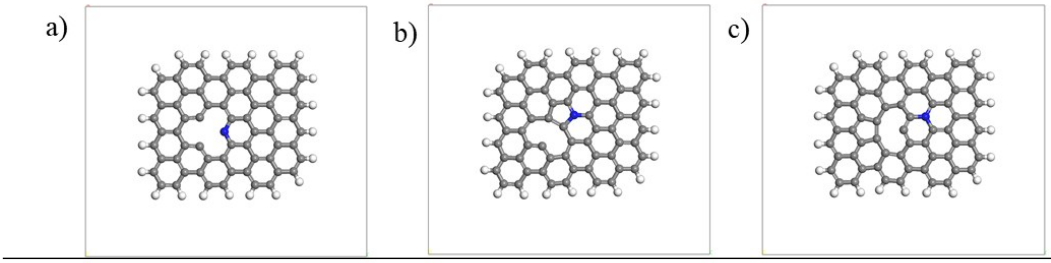

Figure S6. Models of N-PC: a) pyridinic N and b), c) graphitic N.

Table S4. Relative energies of N-PC.

	a	**b**	**c**
Relative energies of N-PC/eV	0	0.15	0.58
Adsorption energies for Mo atom/eV	-6.98	-6.35	-6.61

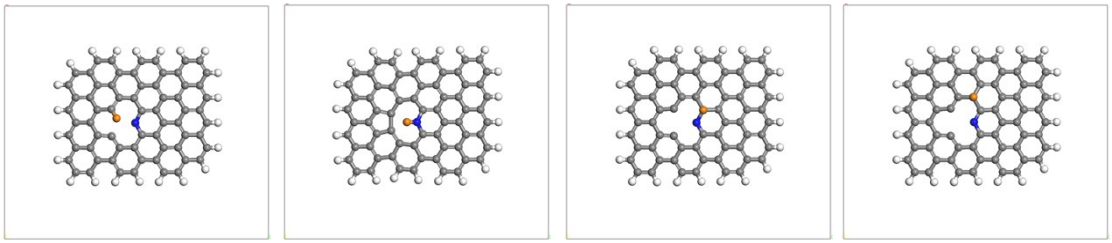

Figure S7. Configurations of H* adsorption on N-PC.

Table S5. H* adsorption energy and Gibbs free energy on N-PC.

	a	**b**	**c**	**d**
E_{ads}	-2.28	-2.94	1.11	0.34
ΔG	-2.00	-2.66	1.39	0.62

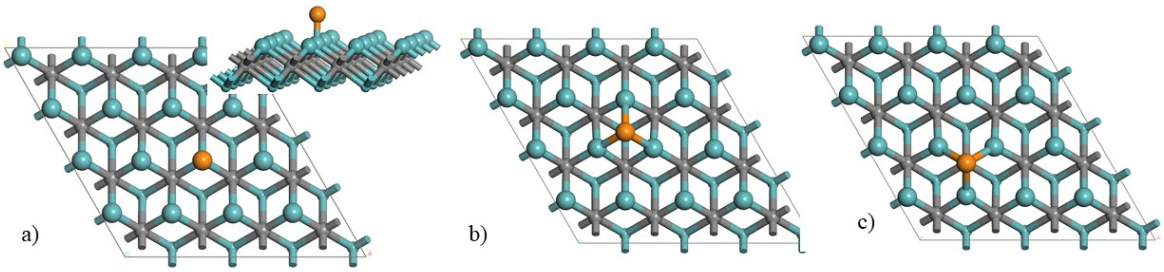

Figure S8. Model structures of H* adsorption on the different adsorption sites of (001) surface of β-Mo_2C: a) adsorbed at the top of Mo atom; b) and c) adsorbed at the hole. (Atom colors: grey: C, cyan: Mo, orange: H).

Table S6. H* adsorption energy and Gibbs free energy of possible active sites for Mo_2C (001) surface.

	a	**b**	**c**
E_{ads}/eV	-0.46	-0.87	-0.77
ΔG_{H*}/eV	-0.18	-0.59	-0.49

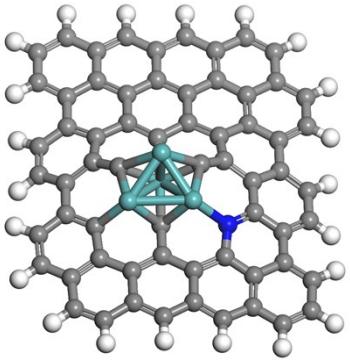

Figure S9. Models of Mo_4 cluster embed on N-PC.

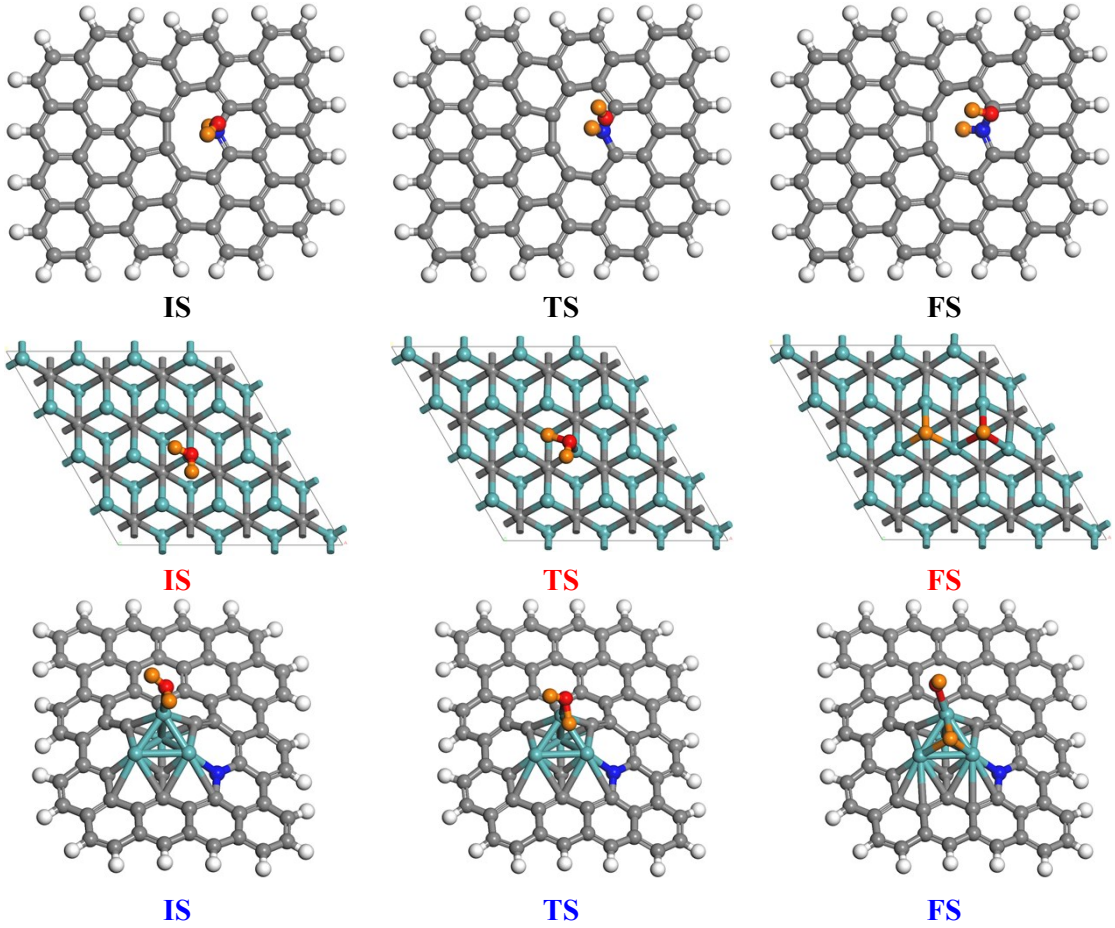

Figure S10. The detail structures of H_2O dissociation on N-PC, Mo_2C (001) surface and Mo_2C/N-PC.

References

1. H. Lin, Z. Shi, S. He, X. Yu, S. Wang, Q. Gao and Y. Tang, *Chem. Sci.*, 2016, **7**, 3399-3405.
2. C. Wu and J. Li, *ACS App. Mater. Inter.*, 2017, **9**, 41314-41322.
3. L. Zhang, H. Yang, D. K. J. A. Wanigarathna and B. Liu, *Small Methods*, 2018, **2**, 1700353.
4. J. S. Kang, J. Kim, M. J. Lee, Y. J. Son, D. Y. Chung, S. Park, J. Jeong, J. M. Yoo, H. Shin, H. Choe, H. S. Park and Y. E. Sung, *Adv Sci (Weinh)*, 2018, **5**, 1700601.
5. Y. Huang, Q. Gong, X. Song, K. Feng, K. Nie, F. Zhao, Y. Wang, M. Zeng, J. Zhong and Y. Li, *Acs Nano*, 2016, **10**, 11337-11343.
6. M. A. R. Anjum, M. H. Lee and J. S. Lee, *ACS Catal.*, 2018, **8**, 8296-8305.
7. J.-Q. Chi, W.-K. Gao, J.-H. Lin, B. Dong, J.-F. Qin, Z.-Z. Liu, B. Liu, Y.-M. Chai and C.-G. Liu, *J. Catal.*, 2018, **360**, 9-19.