Supplementary Information

## Synergistic effect of S vacancy and P dopants in MoS<sub>2</sub>/Mo<sub>2</sub>C to promote

## electrocatalytic hydrogen evolution

Yaru Zhao <sup>a</sup>, Wang Xin <sup>a, b</sup>, Bitao Liu <sup>a, b</sup>, Hongxing Li <sup>a</sup>, Yuqing Xu <sup>a, b</sup>, Zixuan Zhang <sup>a</sup>

<sup>a</sup> College of Physics and Optoelectronics Technology, Baoji University of Arts and Sciences, Baoji 721016, China

<sup>b</sup> Research Institute for New Materials Technology, Chongqing University of Arts and Sciences, Chongqing, 402160,

China

Correspondence author. E-mail: liubitao007@163.com (B.T. Liu)

## Contents

Figure S11
Figure S21
Figure S32
Figure S4
Figure S54
Figure S64
Figure S75
Figure S8
Figure S9
Figure S107
Figure S117
Figure S12
Figure S13
Figure S149
Figure S15
Figure S1610
Table S111
Reference



Figure S1. SEM image of Mo-MoF.



Figure S2. SEM image of Mo<sub>2</sub>C.



Figure S3. SEM image of different phosphating temperature (a,b) 600°C; (c,d) 700 °C; (e,f) 900 °C.



Figure S4. SEM image of different phosphorus content at 800 °C (a,b) 0.05g; (c,d) 0.2g; (e,f) 0.3g.



Figure S5. XRD patterns of different phosphating temperature (900°C, 800°C, 700°C, 600°C).



Figure S6. EDS spectra of P-MoS<sub>2</sub>/Mo<sub>2</sub>C.



Figure S7. EDS elemental mappings of  $MoS_2/Mo_2C$ .



Figure S8. (a, b) TEM images and (c) HR-TEM image of P<sub>900</sub>-MoS<sub>2</sub>/Mo<sub>2</sub>C (d) corresponding EDS elemental mappings of P<sub>900</sub>-MoS<sub>2</sub>/Mo<sub>2</sub>C; (e) EDX spectra of P<sub>900</sub>-MoS<sub>2</sub>/Mo<sub>2</sub>C.



Figure S9. C 1s XPS of P-MoS<sub>2</sub>/Mo<sub>2</sub>C, MoS<sub>2</sub>/Mo<sub>2</sub>C and Mo<sub>2</sub>C.



Figure S10. XPS of Mo 3d in different phosphating temperature (700°C, 800°C, 900°C).



Figure S11. XPS of P 2p in different phosphating temperature (700°C, 800°C, 900°C)



Figure S12. XPS of S 2p in different phosphating temperature (700°C, 800°C, 900°C)



Figure S13. HER polarization curves tested at different phosphating temperature (900°C, 800°C, 700°C, and 600 °C) in 1 M KOH.



Figure S14. HER polarization curves tested of different phosphorus content (0.05, 0.1, 0.2, and 0.3 g) at 800°C.



Figure S15. HER polarization curves tested of Mo<sub>2</sub>C and Mo MOF.



Figure S16. Typical cyclic voltammograms at different scan rates from 20 to 100 mV s<sup>-1</sup>. (a) P-MoS<sub>2</sub>/Mo<sub>2</sub>C; (b) H<sub>2</sub>-MoS<sub>2</sub>/Mo<sub>2</sub>C; (c) MoS<sub>2</sub>/Mo<sub>2</sub>C-p; (d) N<sub>2</sub>-MoS<sub>2</sub>/Mo<sub>2</sub>C and (e) MoS<sub>2</sub>/Mo<sub>2</sub>C. The scanning potential range is from 1.023 V to 1.223V vs SCE.

		Tafel slope	
Catalyst	η <sub>10</sub> (mV)	(mV dec <sup>-1</sup> )	Reference
P-MoS <sub>2</sub> /Mo <sub>2</sub> C	66	67	This work
H-MoS <sub>2</sub> /MoP	92	59	Small, 2020, 16, 2002482 <sup>1</sup>
N-MoP/CC	70	_	Appl. Catal. B: Environ., (2019) 118441 <sup>2</sup>
MoS2/Mo2C	63	48	ACS Catal.,(2017),7,7312-73183
MoS <sub>2</sub> /CoNi <sub>2</sub> S <sub>4</sub>	78	67.4	Adv. Funct. Mater.,(2019) 1908520 <sup>4</sup>
MoS <sub>2</sub> /NiCoS	189	75	J. Mater. Chem. A, 2019, 7, 27594-27602 <sup>5</sup>
NiS/MoS <sub>2</sub>	174	70.2	J. Mater. Chem. A, 2019,7,21514-21522 <sup>6</sup>
$MoS_2$	153	73	ACS Energy Lett. 2019, 4, 2830-2835 7
CuS@MoS <sub>2</sub>	135	50	J. Colloid Interface Sci., 2020, 564, 77-87 <sup>8</sup>
N-doped MoS <sub>2</sub>	114	46.8	J. Am. Chem. Soc. 2019, 141, 18578-1858 <sup>9</sup>
CoP/CN@MoS2	149	88	ACS Appl. Mater. Interfaces 2019,11, 366 <sup>10</sup>

Table S1. Summary of various MoS<sub>2</sub>-based catalysts for HER in 1 M KOH.

## References

- Q. Liu, Z. Xue, B. Jia, Q. Liu, K. Liu, Y. Lin, M. Liu, Y. Li and G. Li, Hierarchical nanorods of MoS<sub>2</sub>/MoP heterojunction for efficient electrocatalytic hydrogen evolution reaction, *Small*, 2020, 16, 2002482.
- 2. C. G. López-Calixto, M. Liras, V. A. de la Peña O'Shea and R. Pérez-Ruiz, Synchronized biphotonic process triggering CC coupling catalytic reactions, Applied Catalysis B: Environmental, 2018, **237**, 18-23.
- Z. Zhao, F. Qin, S. Kasiraju, L. Xie, M.Alam, Vertically Aligned MoS<sub>2</sub>/Mo<sub>2</sub>C hybrid Nanosheets Grown on Carbon Paper for Efficient Electrocatalytic Hydrogen Evolution, ACS Catal., 2017, 7, 7312-7318.
- 4. J. Hu, C. Zhang, P. Yang, J. Xiao, T. Deng, Z. Liu, B. Huang, M. K. H. Leung and S. Yang, Kinetic-Oriented Construction of MoS 2 Synergistic Interface to Boost pH-Universal Hydrogen Evolution, Adv. Funct. Mater., 2019, **30**, 1908520.
- 5. C. Qin, A. Fan, X. Zhang, S. Wang, X. Yuan and X. Dai, Interface engineering: few-layer MoS<sub>2</sub> coupled to a NiCo-sulfide nanosheet heterostructure as a bifunctional electrocatalyst for overall water splitting, Journal of Materials Chemistry A, 2019, 7, 27594-27602.
- 6. A. Long, W. Li, M. Zhou, W. Gao, B. Liu, J. Wei, X. Zhang, H. Liu, Y. Liu and X. Zeng, MoS<sub>2</sub> nanosheets grown on nickel chalcogenides: controllable synthesis and electrocatalytic origins for the hydrogen evolution reaction in alkaline solution, Journal of Materials Chemistry A, 2019, 7, 21514-21522.
- 7. H. A. Ariyanta, T. A. Ivandini and Y. Yulizar, A novel way of the synthesis of three-dimensional (3D) MoS<sub>2</sub> cauliflowers using allicin, Chem. Phys. Lett., 2021, **767**, 138345.
- L. Liu, X. Liu and S. Jiao, CuS@defect-rich MoS<sub>2</sub> core-shell structure for enhanced hydrogen evolution, J. Colloid Interface Sci., 2020, 564, 77-87.
- H. Wang, X. Xiao, S. Liu, C.-L. Chiang, X. Kuai, C.-K. Peng, Y.-C. Lin, X. Meng, J. Zhao, J. Choi, Y.-G. Lin, J.-M. Lee and L. Gao, Structural and Electronic Optimization of MoS<sub>2</sub> Edges for Hydrogen Evolution, J. Am. Chem. Soc., 2019, 141, 18578-18584.
- J.-G. Li, K. Xie, H. Sun, Z. Li, X. Ao, Z. Chen, K. K. Ostrikov, C. Wang and W. Zhang, Template-Directed Bifunctional Dodecahedral CoP/CN@MoS<sub>2</sub> Electrocatalyst for High Efficient Water Splitting, ACS Appl. Mater. Interfaces, 2019, 11, 36649-36657.