Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Heterointerface Engineering of Trilayer-Shelled Ultrathin MoS_2/MoP/N-doped Carbon Hollow Nanobubbles for Efficient Hydrogen Evolution

Jing-Qi Chi [a, †], Yong-Ming Chai [a, †], Xiao Shang [a], Bin Dong [*a], Chen-Guang Liu [a], Wenjun Zhang [b], Zhong Jin [*b]

a State Key Laboratory of Heavy Oil Processing, College of Science, China University of Petroleum (East China), Qingdao 266580, PR China

b Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China

*** Corresponding Authors.** Email: dongbin@upc.edu.cn (B. Dong), zhongjin@nju.edu.cn (Z. Jin)

† These authors contributed equally to this work.

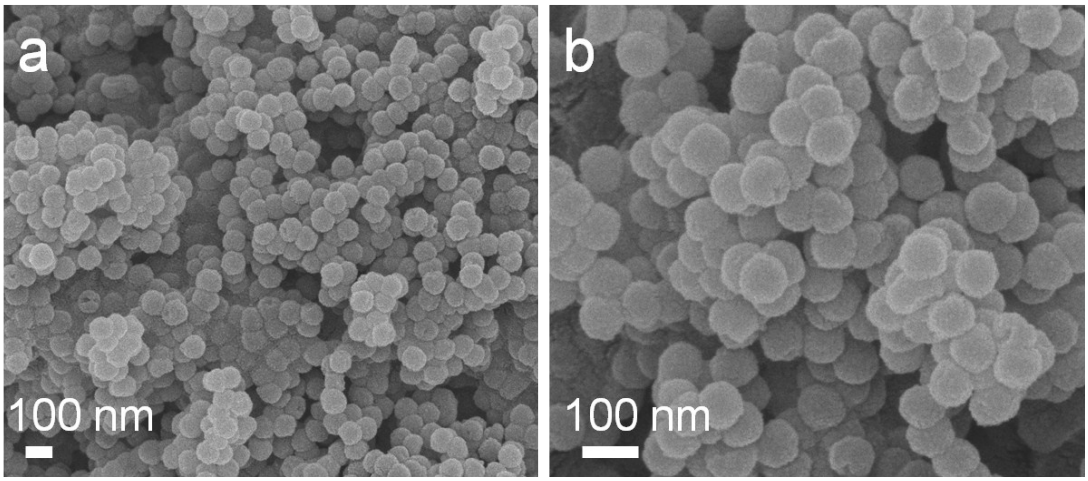

Fig. S1 (a,b) SEM images of NC nanospheres.

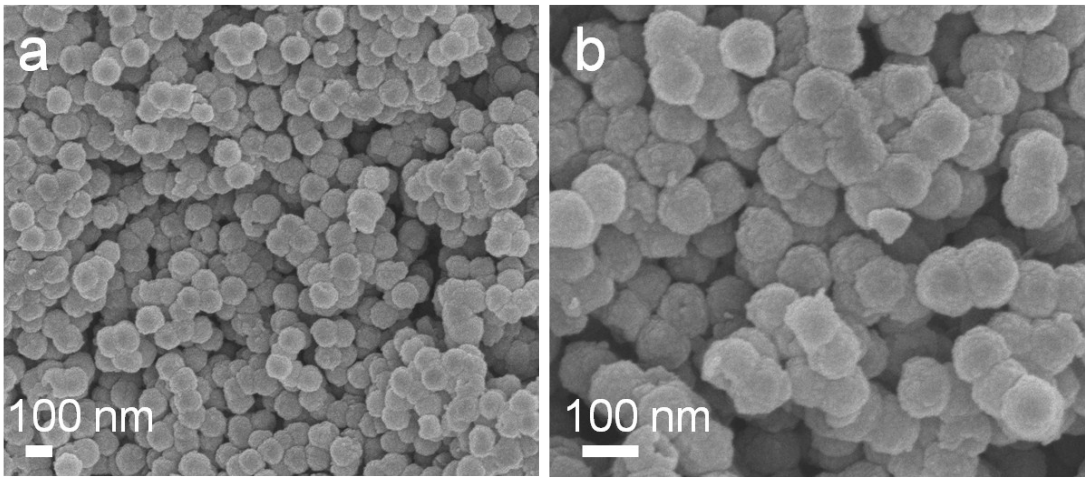

Fig. S2 (a,b) SEM images of MoS_2/NC nanobubbles.

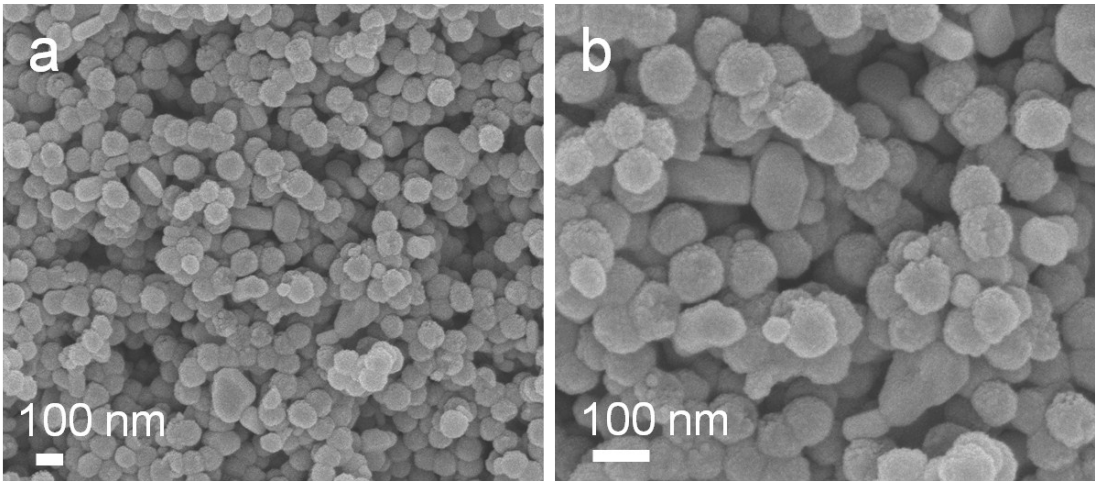

Fig. S3 (a,b) SEM images of MoP/NC nanobubbles.

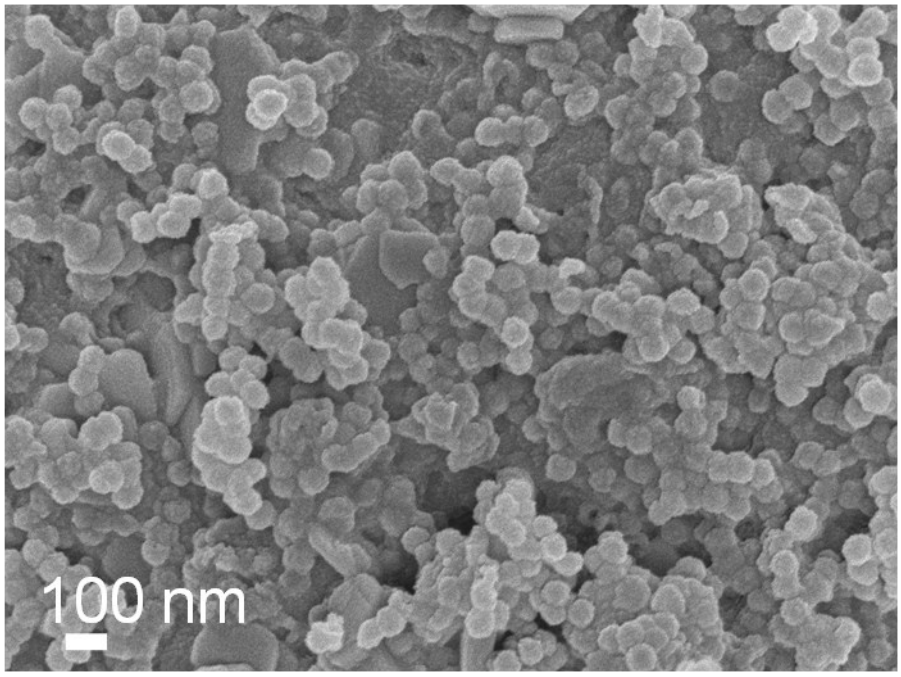

Fig. S4 SEM image of MoS_2/MoP/NC.

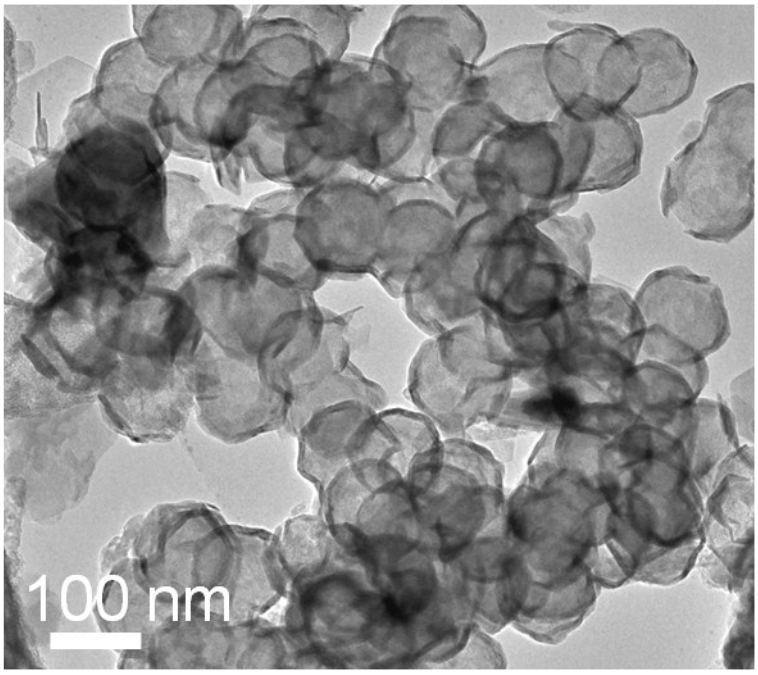

Fig. S5 TEM image of MoS_2/MoP/NC nanobubbles.

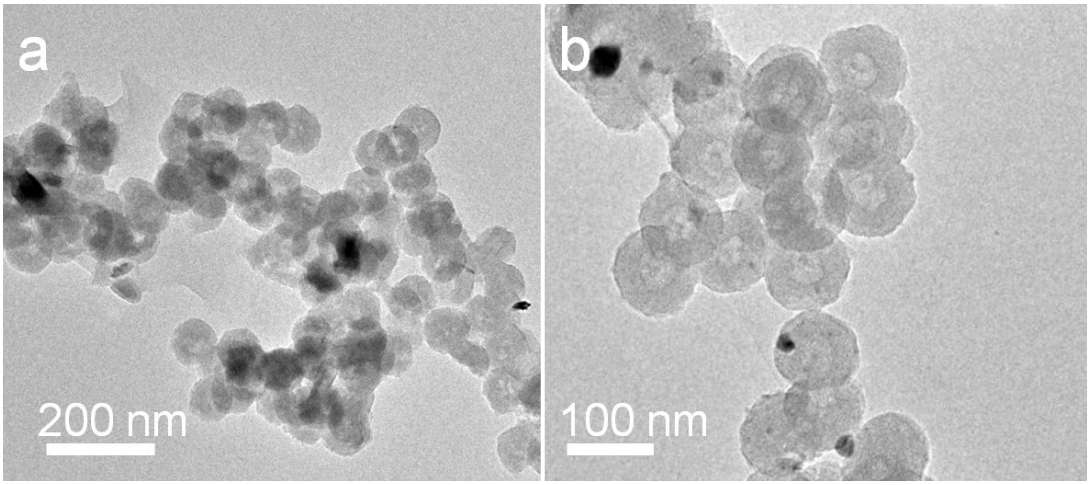

Fig. S6 (a,b) TEM images of NC nanospheres.

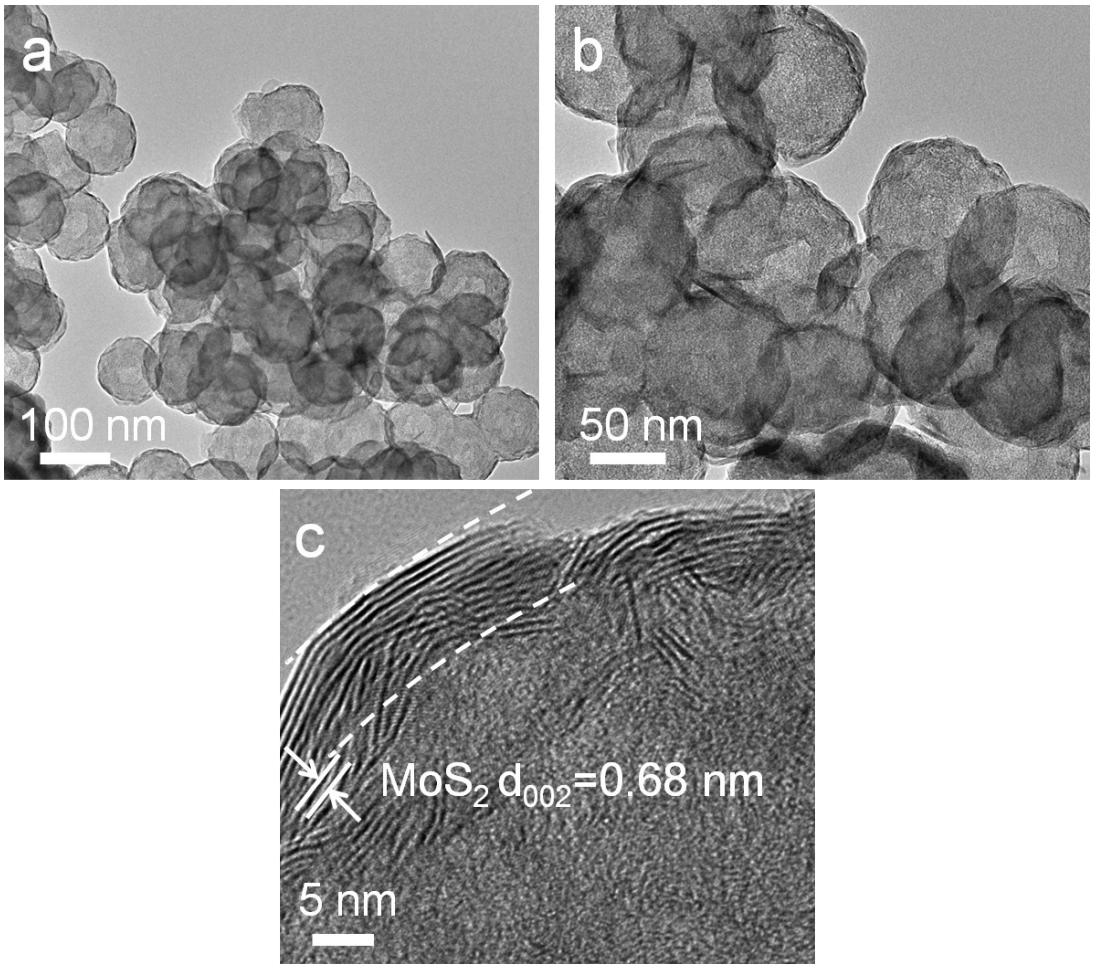

Fig. S7 (a,b) TEM and (c) HRTEM images of MoS_2/NC nanobubbles.

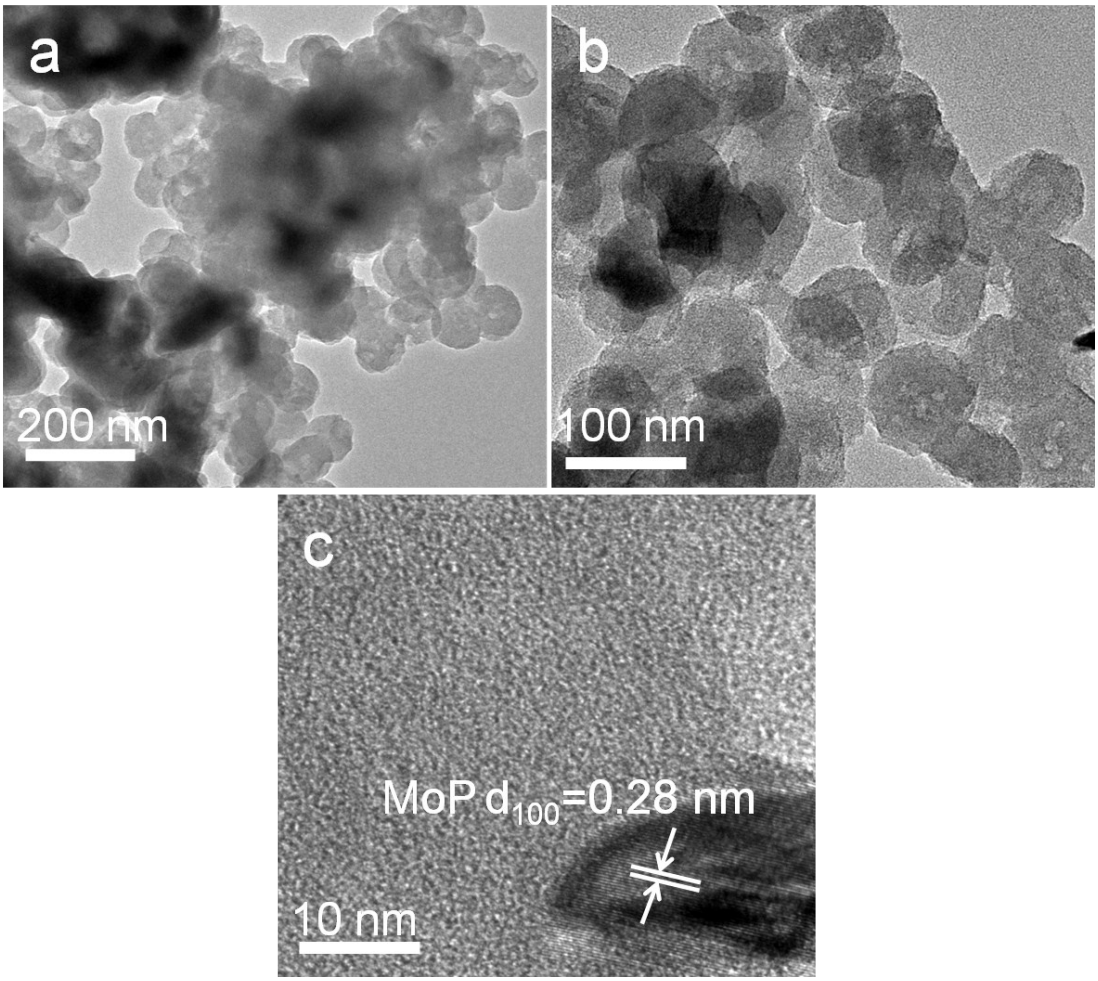

Fig. S8 (a,b) TEM and (c) HRTEM images of MoP/NC nanobubbles.

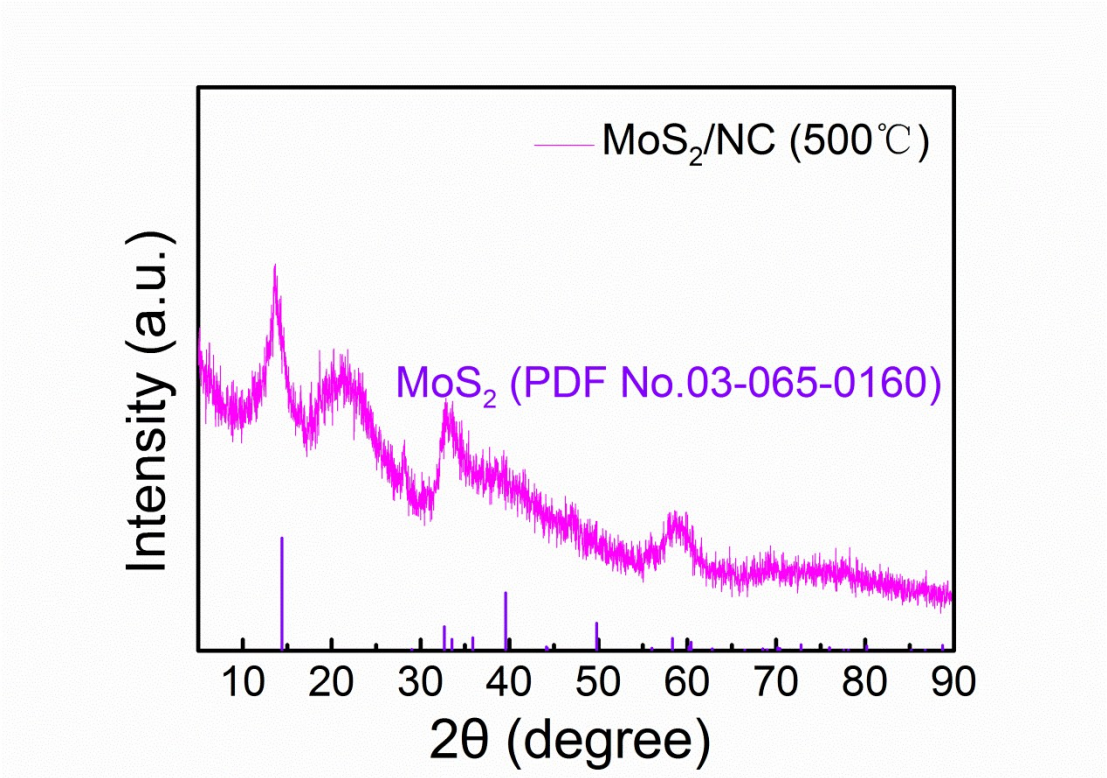

Fig. S9 XRD pattern of MoS_2/NC nanobubbles obtained at 500 °C.

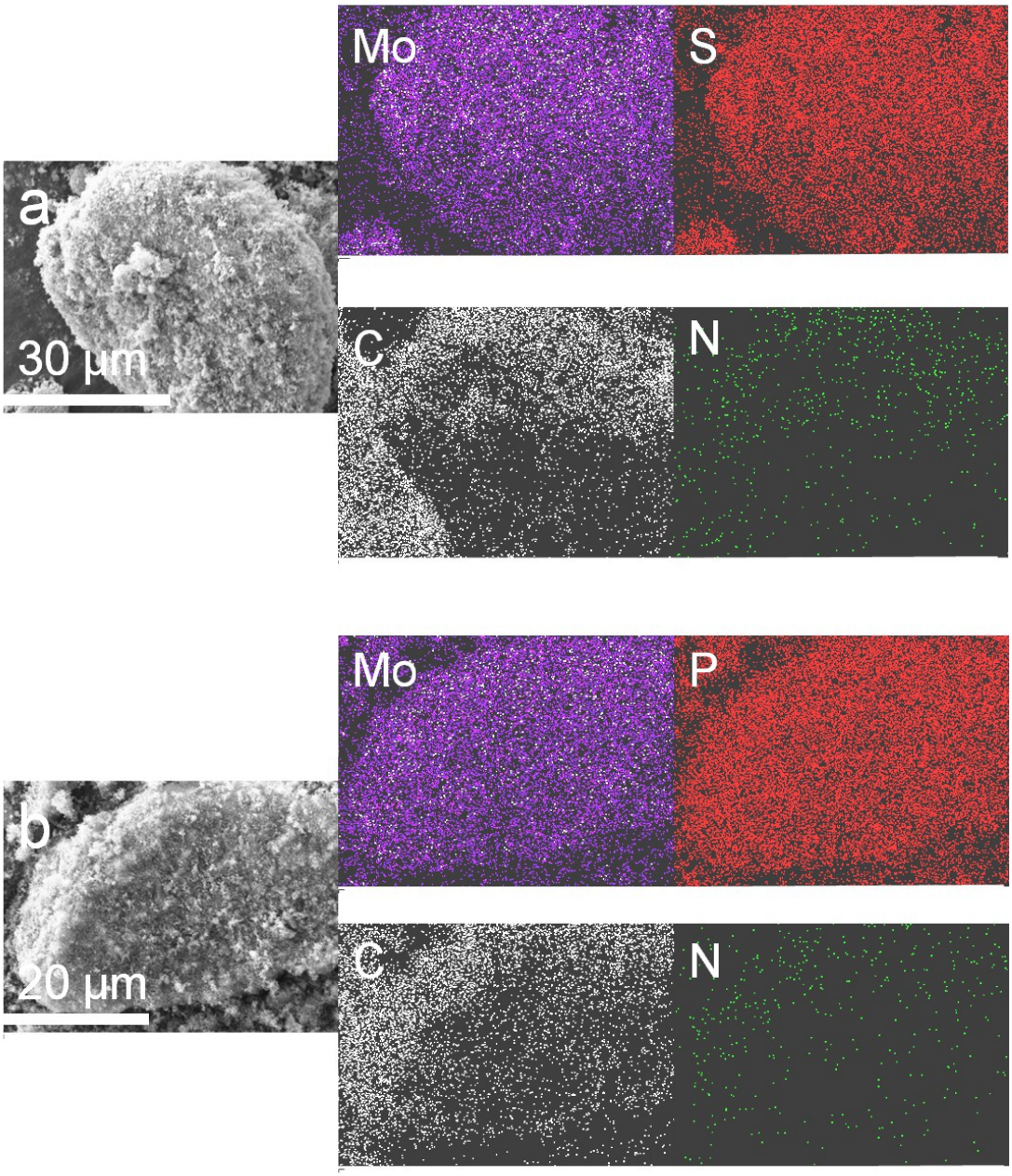

Fig. S10 (a) SEM image and corresponding SEM elemental mappings (Mo, S, C, and N elements) of MoS_2/NC nanobubbles. (b) SEM image and corresponding SEM elemental mappings (Mo, P, C, and N elements) of MoP/NC nanobubbles.

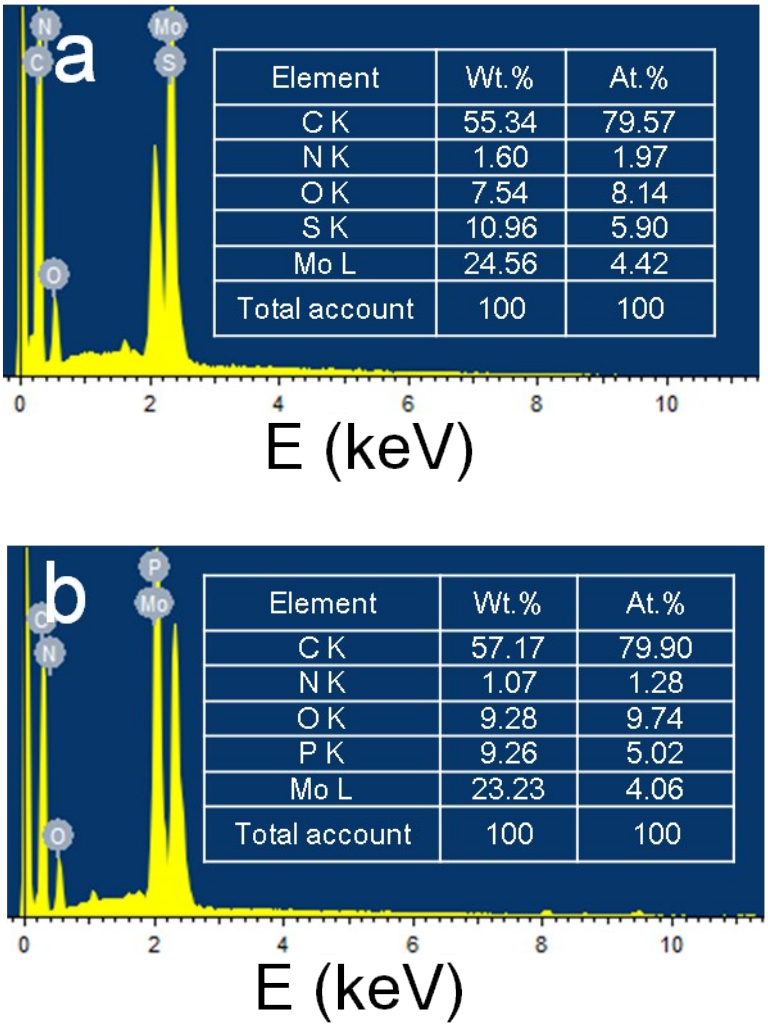

Fig. S11 EDX analysis of (a) MoS_2/NC and (b) MoP/NC nanobubbles.

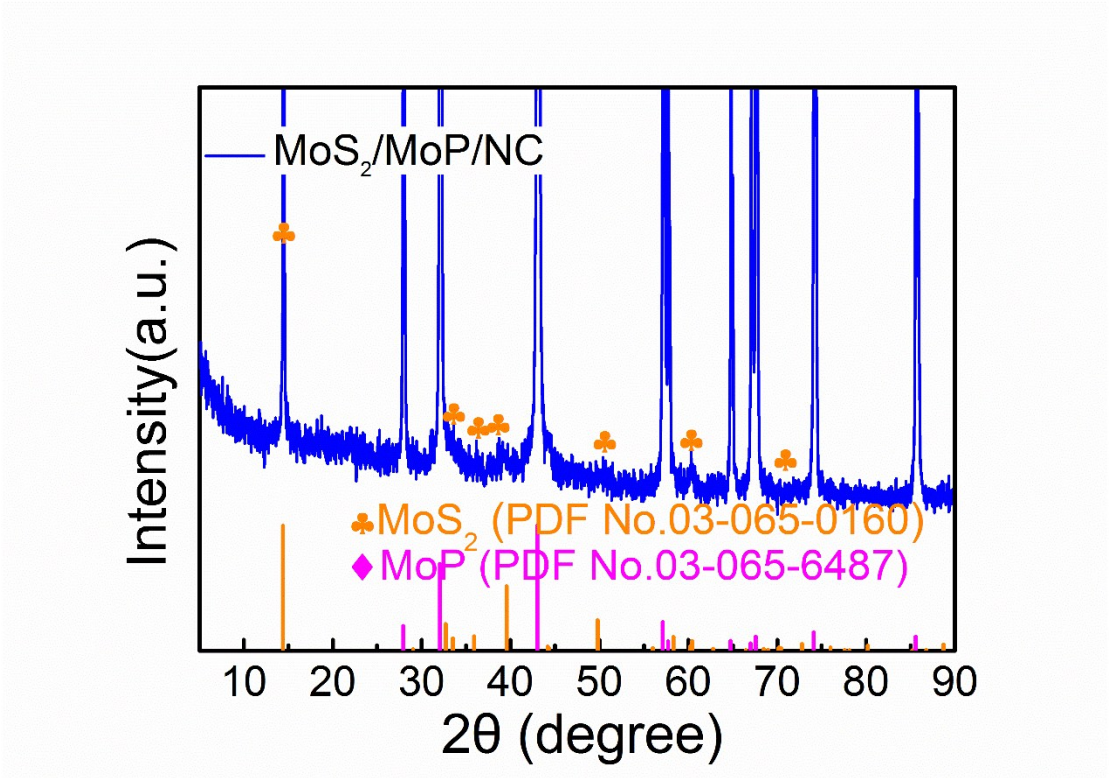

Fig. S12 Enlarged XRD patterns of MoS_2/MoP/NC nanobubbles.

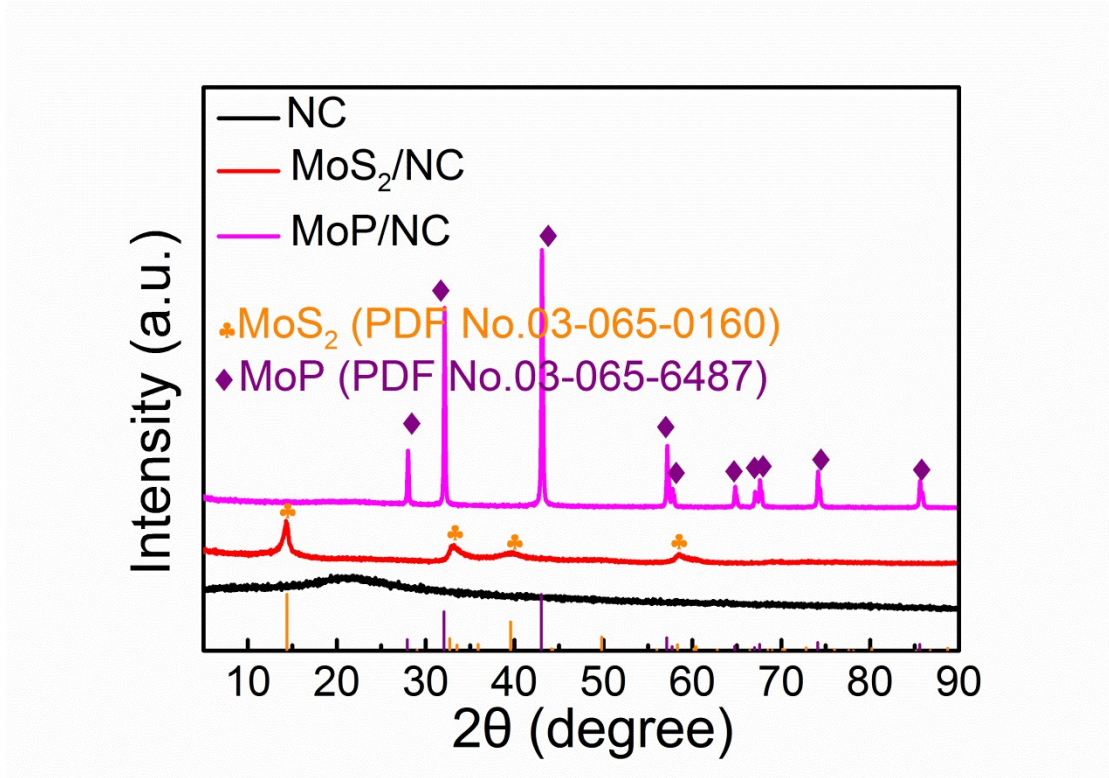

Fig. S13 XRD patterns of NC, MoS_2@NC and MoP/NC nanobubbles.

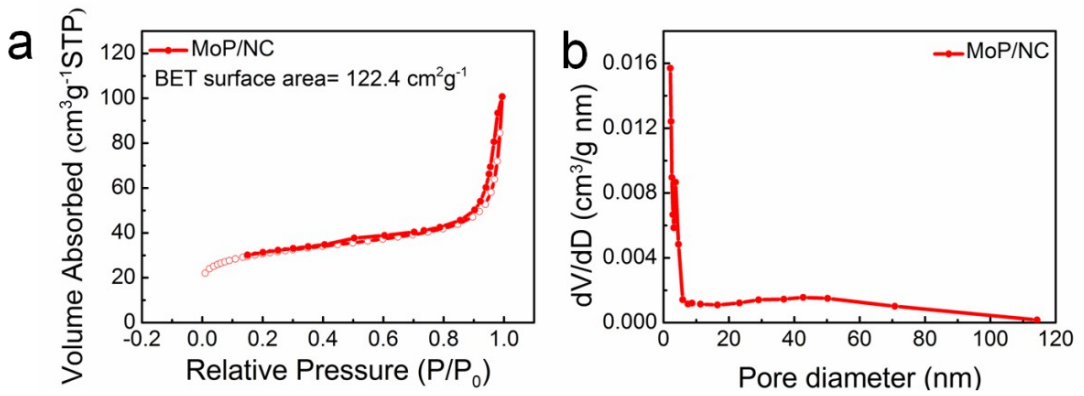

Fig. S14 (a) The N_2 adsorption-desorption isotherm and (b) pore size distribution of MoP/NC nanobubbles.

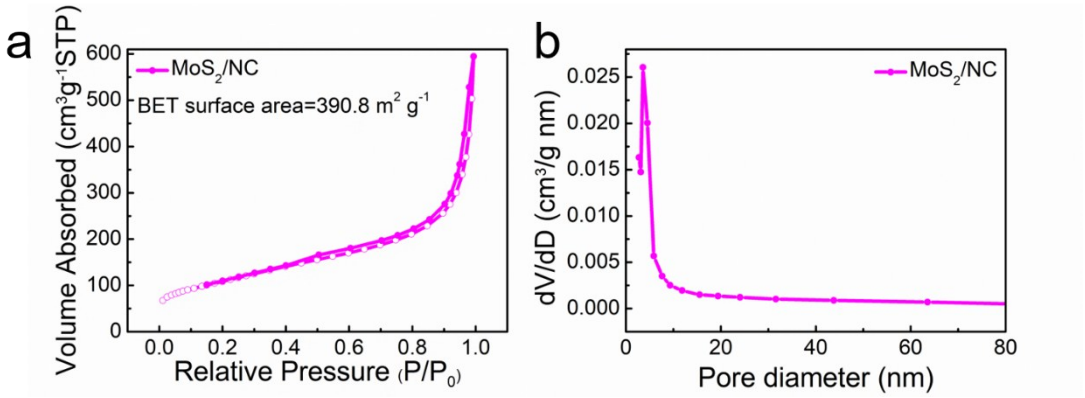

Fig. S15 (a) The N_2 adsorption-desorption isotherm and (b) pore size distribution of MoS_2/NC nanobubbles.

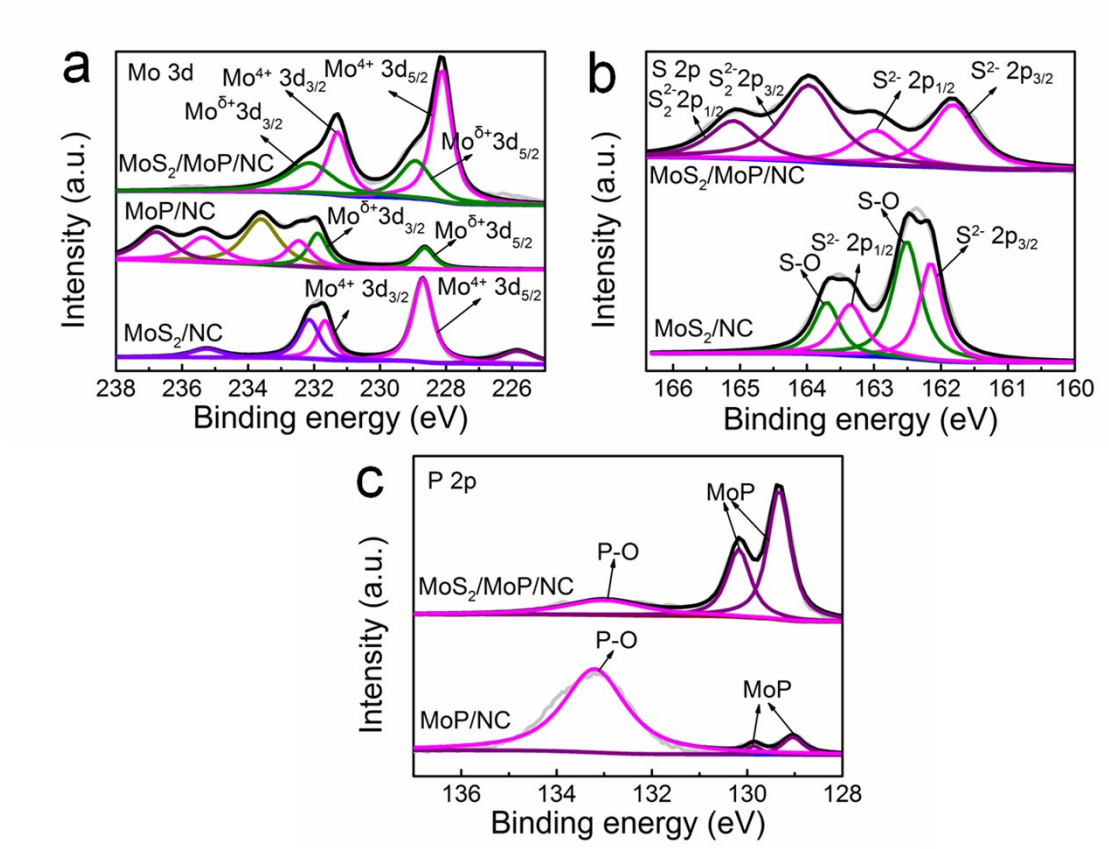

Fig. S16 (a) High-resolution XPS scans at Mo 3d region of MoS_2/MoP/NC, MoP/NC and MoS_2/NC nanobubbles. (b) High-resolution XPS scans at S 2p regions of MoS_2/MoP/NC and MoS_2/NC nanobubbles. (c) High-resolution XPS scans at P 2p regions of MoS_2/MoP/NC and MoP/NC nanobubbles.

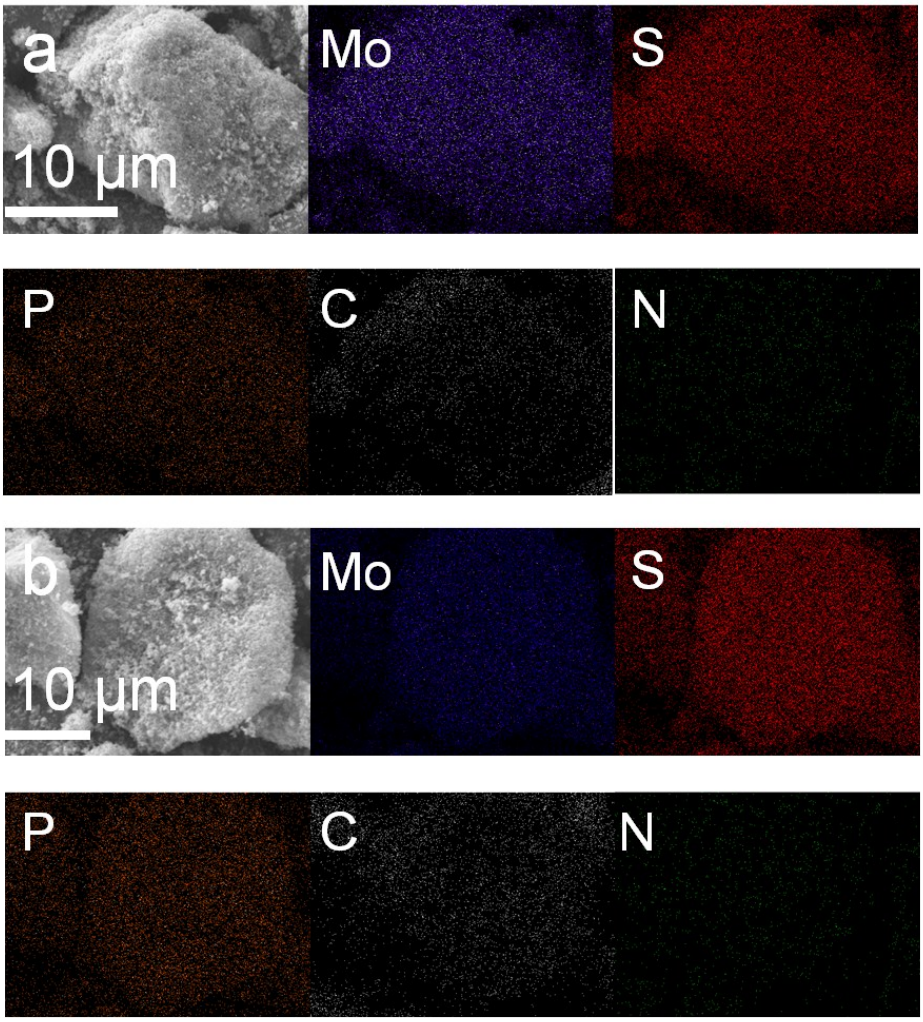

Fig. S17 (a) SEM image and corresponding EDX elemental mappings (Mo, S, P, C and N) of MoS_2/MoP/NC nanobubbles obtained at 800 °C. (b) SEM image and corresponding SEM elemental mappings (Mo, S, P, C and N) of MoS_2/MoP/NC nanobubbles obtained at 1000 °C.

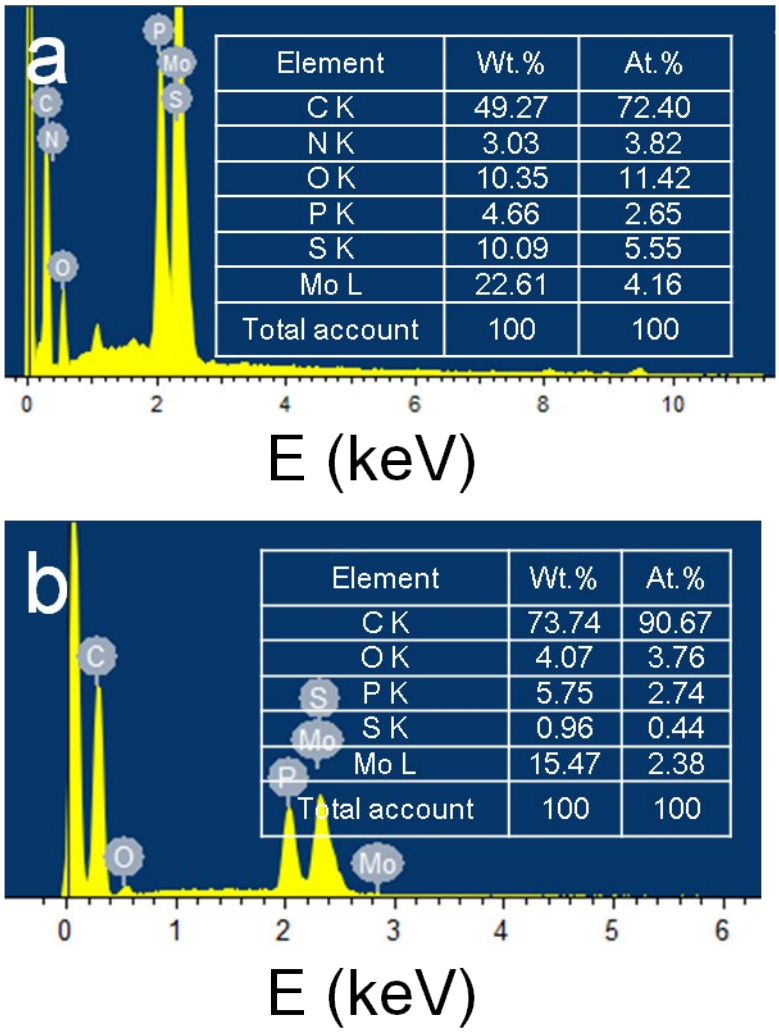

Fig. S18 EDX analysis of MoS_2/MoP/NC obtained at (a) 800 °C) and (b) 1000 °C, respectively.

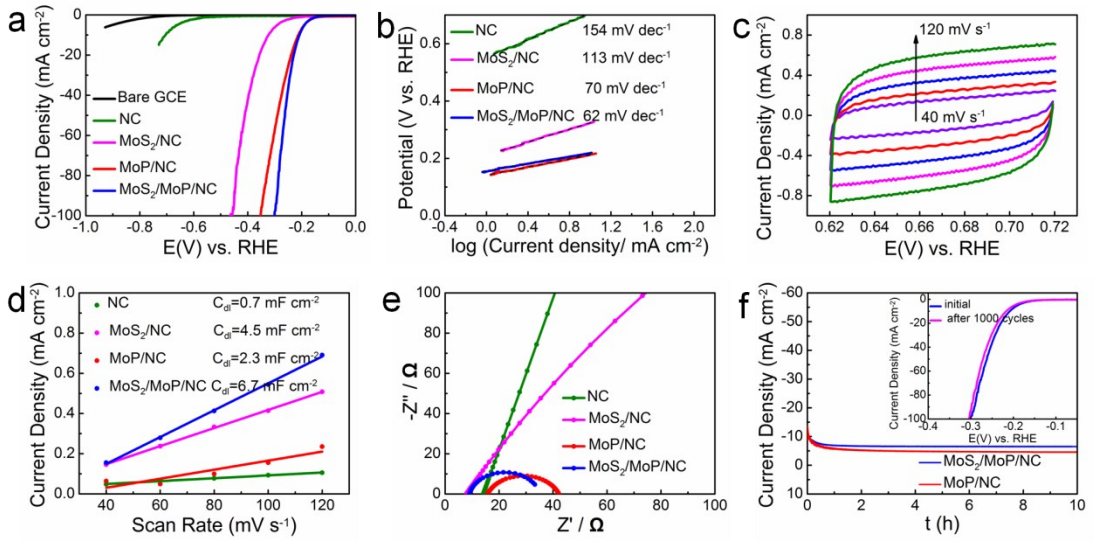

Fig. S19 (a) Polarization curves of bare GCE, NC, MoS_2/NC, MoP/NC and MoS_2/MoP/NC electrodes at a scan rate of 5 mV/s. (b) Tafel plots calculated from (a). (c) Cyclic voltammogram (CV) curves of double-layer capacitance measurement of MoS_2/MoP/NC nanobubbles collected in a selected potential range without Faradic current at different scanning rates (40 - 120 mV s^{-1}). (d) Double-layer capacitances of NC, MoS_2/NC, MoP/NC and MoS_2/MoP/NC nanobubbles. (e) Nyquist plots of NC, MoS_2/NC, MoP/NC and MoS_2/MoP/NC nanobubbles at a potential of -0.15 V (vs. RHE). (f) Chronoamperometry curves of MoP/NC and MoS_2/MoP/NC nanobubbles during HER process over 10 h at a fixed overpotential of 200 mV. The inset of (f) shows the HER polarization curves of MoS_2/MoP/NC nanobubbles before and after 1000 CV cycles from -0.3 to 0.2 V (vs. RHE) in 1.0 M KOH.

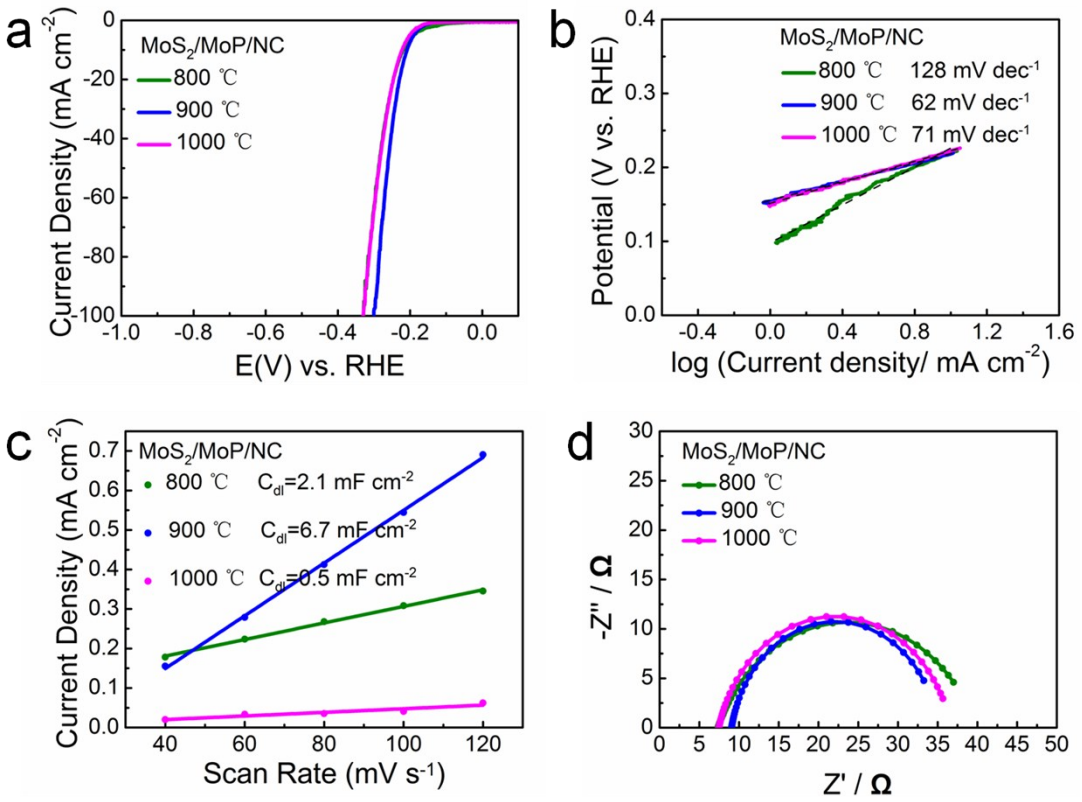

Fig. S20 (a) Polarization curves, (b) Tafel plots, (c) Double-layer capacitance and (d) Nyquist plots of MoS_2/MoP/NC nanobubbles obtained at 800 °C, 900 °C and 1000 measured in 1.0 M KOH, respectively.

Table S1 Comparison of BET surface areas and pore sizes of carbon-based composite electrocatalysts in this work and previous reports.

Electrocatalyst	BET surface area (m^2 g^{-1})	Pore diameter (nm)	Ref.
MoS_2/MoP/NC	954.3	2.4	This work
CoP@NC	367.8	-	1
$Co_6Mo_6C_2$/NCRGO	94.1	4-5	2
Mo_2C@NPC/NPRGO	190	1-2	3
MoC-Mo_2C-31.4	58.5	5.5	4
ß-Mo_2C Nanotubes	127	-	5
Mo_2C@NPC-4	79.3	-	6
Mo_2C/N-C MHNWs	39.3	5.5	7
Mo_2C/NCF	83	-	8
HC800	81.8	-	9
Mo_2C/C(2:2)	101.71	-	10

Table S2 Elemental values of fitted equivalent circuit resistances of NC, MoS_2/NC, MoP/NC and MoS_2/MoP/NC in acidic and alkaline solutions.

Samples	0.5 M H_2SO_4		1.0 M KOH	
	R_s/Ω	R_{ct}/Ω	R_s/Ω	R_{ct}/Ω
NC	11.66	28514	14.16	10661
MoS_2/NC	7.11	921.3	7.67	384.6
MoP/NC	14.4	33.9	15.7	26.4
MoS_2/MoP/NC	6.87	31.36	9.5	25.6

Table S3 Elemental values of fitted equivalent circuit resistances of MoS_2/MoP/NC (800 °C), MoS_2/MoP/NC (900 °C), MoS_2/MoP/NC (1000 °C) in acidic and alkaline solutions.

Samples	0.5 M H_2SO_4		1.0 M KOH	
	R_s/Ω	R_{ct}/Ω	R_s/Ω	R_{ct}/Ω
MoS_2/MoP/NC (800 °C)	6.44	134.8	7.22	37.87
MoS_2/MoP/NC (900 °C)	6.87	31.36	9.5	25.6
MoS_2/MoP/NC (1000 °C)	7.03	165.6	7.22	35.8

References

1 F. Yang, Y. Chen, G. Cheng, S. Chen and W. Luo, *ACS Catal.*, 2017, **7**, 3824-3831.

2 Y. Tang, C. Liu, W. Huang, X. Wang, L. Dong, S. Li and Y. Lan, *ACS Appl. Mater. Interfaces*, 2017, **9**, 16977-16985.

3 J. S. Li, Y. Wang, C. H. Liu, S. L. Li, Y. G. Wang, L. Z. Dong, Z. H. Dai, Y. F. Li and Y. Q. Lan, *Nat. Commun.*, 2016, **7**, 11204.

4 H. Lin, Z. Shi, S. He, X. Yu, S. Wang, Q. Gao and Y. Tang, *Chem. Sci.*, 2016, **7**, 3399-3405.

5 F. Ma, H. Wu, B. Xia, C. Xu and X. W. Lou, *Angew. Chem. Int. Ed.*, 2015, **54**, 15395-15399.

6 L. Ji, J. Wang, L. Guo and Z. Chen, *J. Mater. Chem. A*, 2017, **5**, 5178-5186.

7 L. Yang, X. Li, S. He, G. Du, X. Yu, J. Liu, Q. Gao, R. Hu and M. Zhu, *J. Mater. Chem. A*, 2016, **4**, 10842-10849.

8 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.

9 X. Xu, F. Nosheen and X. Wang, *Chem. Mater.*, 2016, **28**, 6313-6320.

10 C. Wu and J. Li, *ACS Appl. Mater. Interfaces*, 2017, **9**, 41314-41322.