Supporting Information for

**Electrochemical Surface Restructuring of Phosphorus Doped Carbon@MoP Electrocatalysts for Hydrogen Evolution**

Huimin Jiang¹,³, Liting Yan¹,*, Shuo Zhang³, Yanchao Zhao³, Xue Yang¹, Yameng Wang¹, Jianxing Shen¹, Xuebo Zhao¹,³*, Lianzhou Wang²,*

¹School of Materials Science and Engineering, Qilu University of Technology (Shandong Academy of Sciences), No.3501, Daxue Road, Changqing District, Jinan, 250353, P. R. China

²Nanomaterials Centre, School of Chemical Engineering and Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, St Lucia, QLD 4072, Australia

³College of Chemical Engineering, China University of Petroleum (East China), No. 66, West Changjiang Road, Huangdao District, Qingdao, 266580, P. R. China

*Corresponding authors. E-mail: yanlt@qlu.edu.cn (Liting Yan); zhaoxuebo@upc.edu.cn (Xuebo Zhao); l.wang@uq.edu.au (Lianzhou Wang)

S1 Experimental Section

S1.1 Chemicals

Sodium molybdate(VI) dihydrate (Na₂MoO₄·2H₂O), alpha, alpha'-Dibromo-p-xylene (97 wt%), paraformaldehyde (96 wt%), potassium hydroxide (KOH, ≥85.0 wt%), sulfuric acid (95.0~98.0%), hydrochloric acid (36.0~38.0 wt%) and ethanol (≥ 99.7 wt%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Hydrogen bromide (33 wt% in acetic acid) and commercial molybdenum phosphide (99.5%) were purchased from Aladdin. Carbon rod was purchased from Shandong Haike Chemical Group Co., Nafion solution (5 wt% in a mixture of lower aliphatic alcohols and water) and platinum on carbon (Pt/C, 10 wt%) were purchased from Sigma-Aldrich Co. LLC. All reagents were used without further purification.

S1.2 Material Synthesis

S1.2.1 Synthesis of p-xylendenediphosphonic acid (H₄xdp) [S1]:

The ligand was synthesized by reacting alpha, alpha'-Dibromo-p-xylene with triethyl phosphite and followed by refluxing the obtained oil with conc. hydrochloric acid according to the literature method. Block colorless crystals were obtained from the water solution by slow evaporation.

S1.2.2 Synthesis of [(MoO₂)₂(xdp)(H₂O)₂]·2H₂O [S1]

Mo-MOF precursor was prepared according to previous work [S1]. In a typical procedure, Na₂MoO₄·2H₂O (0.240 g, 1.0 mmol) was stirred together with p-xylendenediphosphonic acid (H₄xdp) (0.140 g, 0.5 mmol) in 16ml deionised water. The pH of the solution was adjusted to pH 1 by dropwise addition of conc. hydrochloric acid. The acidified solution was then placed in a 25 cm³ Ace pressure tube and heated at 120 °C for 15 h. The resultant white crystalline material was thoroughly washed with deionised water several times and dried at 80 °C for 12 h under vacuum.
\[ A_{ECSA} = \frac{\text{electrochemical capacitance}}{40 \, \text{MF cm}^{-2}} \text{per cm}^2_{ECSA} \] (S1)
S1.6 Calculated Electrochemically Active Surface Area

MoP@PC:

\[
\text{MoP@PC} = \frac{0.9 \text{ mF cm}^{-2}}{40 \mu \text{F cm}^{-2} \text{ per cm}^2_{\text{ECSA}}} = 22.9 \text{ cm}^2
\]

(S2)

A-MoP@PC:

\[
\text{A-MoP@PC} = \frac{5.2 \text{ mF cm}^{-2}}{40 \mu \text{F cm}^{-2} \text{ per cm}^2_{\text{ECSA}}} = 148.7 \text{ cm}^2
\]

(S3)

S1.7 DFT Calculations

All calculations were performed using Vienna Ab-initio Simulation Package (VASP) of MedeA software, the generalized gradient approximation (GGA) of Perdew–Becke–Ernzerhof (PBE) is used for the exchange-correlation functional [S3-S5] The MoP@C\textsubscript{240} model was built by encapsulating a MoP cluster with a graphitic carbon cage C\textsubscript{240}, which performed well in previous study [S6, S7]. In the construction of model MoP@C\textsubscript{239}P\textsubscript{1}, and C\textsubscript{239}P\textsubscript{1}, P atom was introduced by substituting C atom in the carbon cage. All structures were fully relaxed to the ground state and spin-polarization was considered in all calculations. The convergence of energy and forces were set to $1 \times 10^{-4}$ eV and 0.01 eV Å\textsuperscript{-1}, respectively. An energy cutoff of 400 eV and a Gamma k-point sampling were found to get convergent geometry. For HER, the free energies of the intermediates were obtained by $\Delta G(H^*) = \Delta E(H^*) + \Delta ZPE - T\Delta S$, where $\Delta E(H^*)$, $\Delta ZPE$ and $\Delta S$ is the binding energy, zero-point energy change and entropy change of adsorption H, respectively. The $\Delta ZPE$ and $\Delta S$ were obtained according to the method reported by Norskov [S8, S9].

The adsorption energy ($E_{\text{ads}}$) is given by

\[
E_{\text{ads}} = E_{\text{adsorbed slab + adsorbate}} - (E_{\text{adsorbed slab}} + E_{\text{adsorbate}})
\]

where $E_{\text{adsorbed slab + adsorbate}}$, $E_{\text{adsorbed slab}}$, and $E_{\text{adsorbate}}$ correspond to the total energy of the optimized system, the adsorbed slab, and the isolated adsorbate molecule, respectively.

S2 Supplementary Figures and Tables

![Fig. S1 XRD patterns of Mo-MOF](image_url)
Fig. S2 TGA of Mo-MOF precursor in N₂ atmosphere

Fig. S3 N₂ adsorption/desorption isotherm at 77 K of Mo-MOF

Fig. S4 LSV curves of MoP calcined at 900-1100 °C in 0.5 M H₂SO₄
**Fig. S5** a) N$_2$ adsorption/desorption isotherm at 77 K and b) corresponding NLDFT pore diameter distribution of MoP@PC

**Fig. S6** XPS spectrum of MoP@PC and A-MoP@PC

**Fig. S7** CV curves of A-MoP@PC activation for different time
**Fig. S8** Cyclic voltammograms of a) MoP@PC and b) A-MoP@PC after activation with various scan rates.

**Fig. S9** a) N₂ adsorption/desorption isotherm at 77 K and b) corresponding NLDFT pore diameter distribution of A-MoP@PC.

**Fig. S10** a) and b) SEM image of A-MoP@PC after the stability test.
**Fig. S11** a) TEM and b) HRTEM of A-MoP@PC after the stability test

**Fig. S12** High resolution XPS of a) Mo 3d, b) P 2p, c) C 1s and d) O 1s of A-MoP@PC after the stability test

**Fig. S13** HER polarization curves of MoP@PC activation for different time after addition of 5 mM SCN\(^-\) ions in 0.5 M H\(_2\)SO\(_4\)
**Fig. S14** Chronoamperometric stability test of commercial MoP for HER in **a)** 0.5 M H$_2$SO$_4$ and **b)** 1.0 M KOH

**Fig. S15 a-c** Computational models of C. **d-f** Configurations of adsorbates of structures on C for HER
**Fig. S16** a-c Computational models of PC. d-f Configurations of adsorbates of structures on PC for HER

**Fig. S17** a-c Computational models of A-MoP@C. d-f Configurations of adsorbates of structures on A-MoP@C for HER
Fig. S18  a-c  Computational models of A-MoP@PC.  d-f  Configurations of adsorbates of structures on A-MoP@PC for HER

Fig. S19  Tafel plots of MoP@PC, A-MoP@PC and Pt/C in 1.0 M KOH
**Table S1** Comparison of HER activity for A-MoP@PC and recently reported noble metal-free hydrogen evolution catalysts

| Catalyst                          | $\eta_{10}$ (mV) | Tafel slope (mV dec$^{-1}$) | Electrolyte       | Refs. |
|-----------------------------------|------------------|----------------------------|-------------------|-------|
| N@MoPC$_x$                        | 108              | 69.4                       | 0.5 M H$_2$SO$_4$ | [S2]  |
| MoS$_2$-Me-10%                    | 136              | 37                         | 0.5 M H$_2$SO$_4$ | [S10] |
| WS$_2$                            | 137              | 54                         | 0.5 M H$_2$SO$_4$ | [S11] |
| N-MoS$_2$/CN                      | 114              | 46.8                       | 0.5 M H$_2$SO$_4$ | [S12] |
| Cu3P@NPPC                         | 89               | 76                         | 0.5 M H$_2$SO$_4$ | [S13] |
| meso-Fe-MoS$_2$/CoMo$_2$S$_4$      | 122              | 90                         | 1.0 M KOH         | [S14] |
| O-CoP                             | 98               | 59.9                       | 1.0 M KOH         | [S15] |
| Fe-N$_2$ SAs/NPC                  | 202              | 123                        | 1.0 M KOH         | [S16] |
| NiCoFe@C                          | 260              | 105                        | 1.0 M KOH         | [S17] |
| Mn-doped NiS$_2$/Ni foam          | 71               | 57                         | 1.0 M KOH         | [S18] |
| MoP@NCHSs                         | 92               | 62                         | 1.0 M KOH         | [S19] |
| 0.02Ni–MoP                        | 102              | 58.1                       | 0.5 M H$_2$SO$_4$ |       |
|                                  | 162              | 102.6                      | 1.0 M KOH         |       |
| Fe$_3$C-Co/NC                     | 298              | 100.3                      | 0.5 M H$_2$SO$_4$ |       |
|                                  | 238              | 108.8                      | 1.0 M KOH         |       |
| CoP/NiCoP NTs                     | 125              | 71                         | 0.5 M H$_2$SO$_4$ |       |
|                                  | 133              | 88                         | 1.0 M KOH         |       |
| np-\(\eta\)-MoC NSs              | 122              | 53                         | 0.5 M H$_2$SO$_4$ |       |
|                                  | 119              | 39                         | 1.0 M KOH         |       |
| MoP@NPSC                          | 71               | 75                         | 0.5 M H$_2$SO$_4$ |       |
|                                  | 50               | 45                         | 1.0 M KOH         |       |
| Ti-MoP                            | 93.6             | 44.5                       | 0.5 M H$_2$SO$_4$ |       |
| MoP/CDs                           | 70               | 77.49                      | 1.0 M KOH         |       |
| P-MoP/Mo$_3$N                     | 89               | 53                         | 0.5 M H$_2$SO$_4$ |       |
|                                  | 89               | 78                         | 1.0 M KOH         |       |
| N-MoP-800                         | 175              | 69                         | 0.5 M H$_2$SO$_4$ |       |
|                                  | 125              | 69                         | 1.0 M KOH         |       |
| Ni$_3$P/MoP-CC                    | 290              | 63                         | 0.5 M H$_2$SO$_4$ |       |
|                                  | 78               | 64                         | 1.0 M KOH         |       |
| A-MoP@PC                          | **68**           | **41**                     | 0.5 M H$_2$SO$_4$ | This work |
|                                  | **67**           | **40**                     | 1.0 M KOH         |       |

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