Supporting Information

# Nanostructured Pt-doped Molybdenum Nitrides for Efficient Hydrogen Evolution Reaction

## Experimental Section

### Chemicals

Molybdenum powder (99.0%), Ammonium hexachloropalladate (IV) ($(NH_4)_2PdCl_6$, 99.9%), Chloroplatinic acid ($H_2PtCl_6$, Pt ⩾37.5%), Ruthenium chloride hydrate ($RuCl_3 \cdot xH_2O$,35.0-42.0% Ru basis) and Gold chloride trihydrate ($HAuCl_4$, ⩾99.9%) were purchased from Sigma-Aldrich Chemicals Ltd.. All reagents were directly used without any purification. Nafion solution (5% w/w in water and 1-propanol) was obtained from Alfa Aesar. 20 wt% Pt/C was obtained from Shanghai Hesen Electric Co., Ltd. Carbon paper (TGP-h-060, Toray) were used.

### Synthesis of $MoO_3$

$MoO_3$ nanobelts were synthesized according to a previous reported process with slight modification (see the Supporting Information for details) [1].

### Synthesis of $MoN_x$

Briefly, the as-obtained $MoO_3$ nanobelts (200 mg) were placed in a tube furnace and ammoniated under $NH_3$ atmosphere (100 mL min$^{-1}$) at 750 $^{o}$C for 5 h with a ramping rate of 10 $^{o}$C min$^{-1}$. After cooled down naturally to room temperature in $NH_3$, black products were collected.

### Synthesis of $Pt/MoN_x$

In a typical experiment, $MoN_x$ powder (100 mg) was dispersed in 5mL of water, and then a certain amount of $H_2PtCl_6$ solution (10 mg/mL) was added with magnetic stirring. After being stirred for 2 h, the sample was transferred to a glass dish and subsequently subjected for freeze-drying. Then, the precursor was placed in a crucible and heated to 400 °C at a rate of 5 °C $min^{-1}$ in $H_2$/Ar (5 wt%) and kept at this temperature for 3 h. Catalysts with different Pt weight loadingwere prepared using similar protocols. The as-prepared samples were denoted as Pt-0.5(0.5%), Pt-1(1%), Pt-3(3%), Pt-5(5%), and Pt-7(7%)

**Synthesis of Pd/$MoN_x$, Au/$MoN_x$, Ru/ $MoN_x$**

Pd/$MoN_x$, Au/$MoN_x$ and Ru/$MoN_x$ were synthesized using the same method as that of Pt-5 except that $(NH_4)_2PdCl_6$, $HAuCl_4$, or $RuCl_3$ were added, respectively.

## Characterization

The crystal structure and morphology of the as-synthesized samples were characterized by X-ray diffractometer (XRD) with Cu Kα radiation (λ = 0.154598 nm), scanning electron microscopy (Verios 460L, FEI) and transmission electron microscopy with energy dispersive X-ray spectroscopy (EDS) analysis (TECNAI G2 and FEI Talos F200X). The chemical composition and valence state were characterized by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi). The calibration of the binding energies of the C 1s main peak at 284.8 eV was used.

## Electrochemical measurements

The HER electrocatalytic measurements were performed in a CHI 760E electrochemical workstation, using a three-electrode system in $N_2$ saturated 0.5 M $H_2SO_4$. Ag/AgCl electrode (in saturated KCl solution) and graphite rod were used as reference and counter electrodes, respectively. To prepare the catalyst ink, 5.0 mg catalyst was dispersed in a solution containing 480 μl ethanol and 20 μl 5% Nafion solution. After 3 h ultrasonication, 40 μl catalyst ink was painted on a carbon paper (1 cm×1 cm), and then dried naturally. For comparison, Pt/C (20 wt% Pt, Johnson Matthey) ink was prepared in the same way. The loading of catalyst was 0.4 mg $cm^{-2}$.

Polarization curves were obtained with linear sweep voltammetry at a scan rate of 5 mV $s^{-1}$. All potentials were referenced to the reversible hydrogen electrode (RHE) through the equation: E(RHE) = E(Ag/AgCl) + 0.198 + 0.059 × pH.

Electrochemical impedance spectroscopy (EIS) measurements were carried out from 0.1 Hz to 100 kHz with an amplitude of 50 mV. All data were recorded without iR compensation. The cyclic voltammograms (CV) were tested in a non-faradaic region from 0.224 to 0.424 V versus RHE with scan rates of 5, 10, 20, 40, and 80 mV $s^{-1}$. The electrochemically active surface area (ECSA) was estimated by the double-layer capacitance ($C_{dl}$) method which was measured by CV with various scan rate.

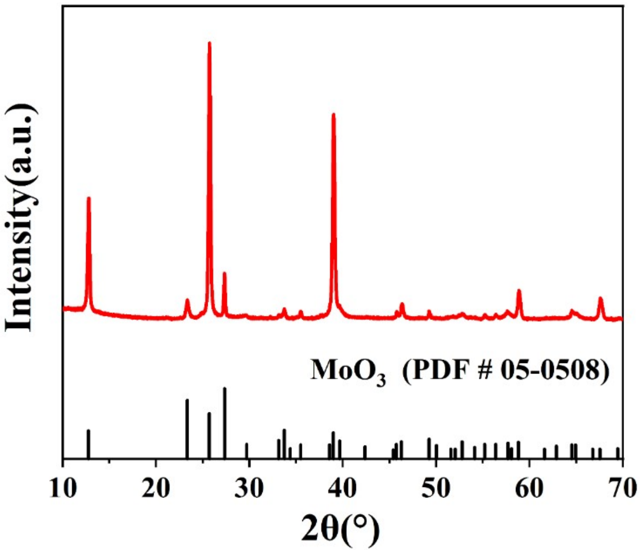

Fig.S1 XRD pattern of $MoO_3$

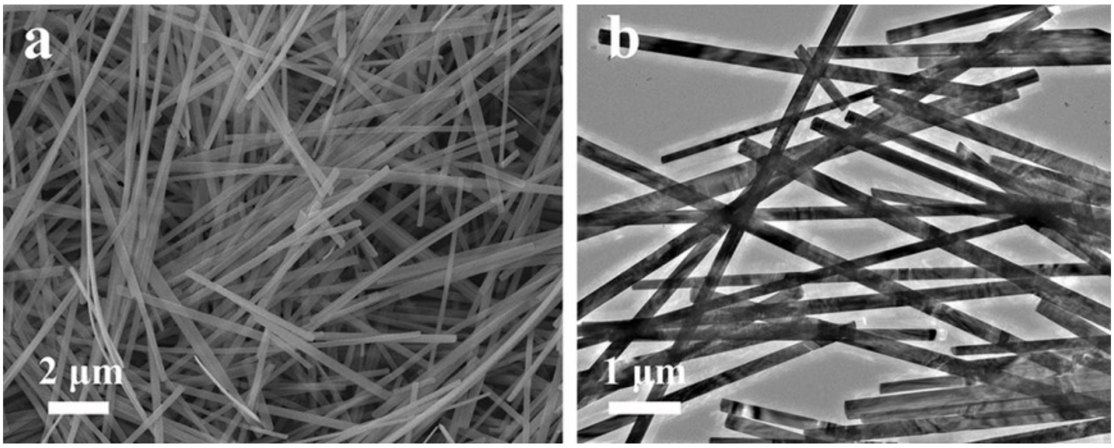

Fig.S2 SEM image (a) and TEM image (b) of $MoO_3$

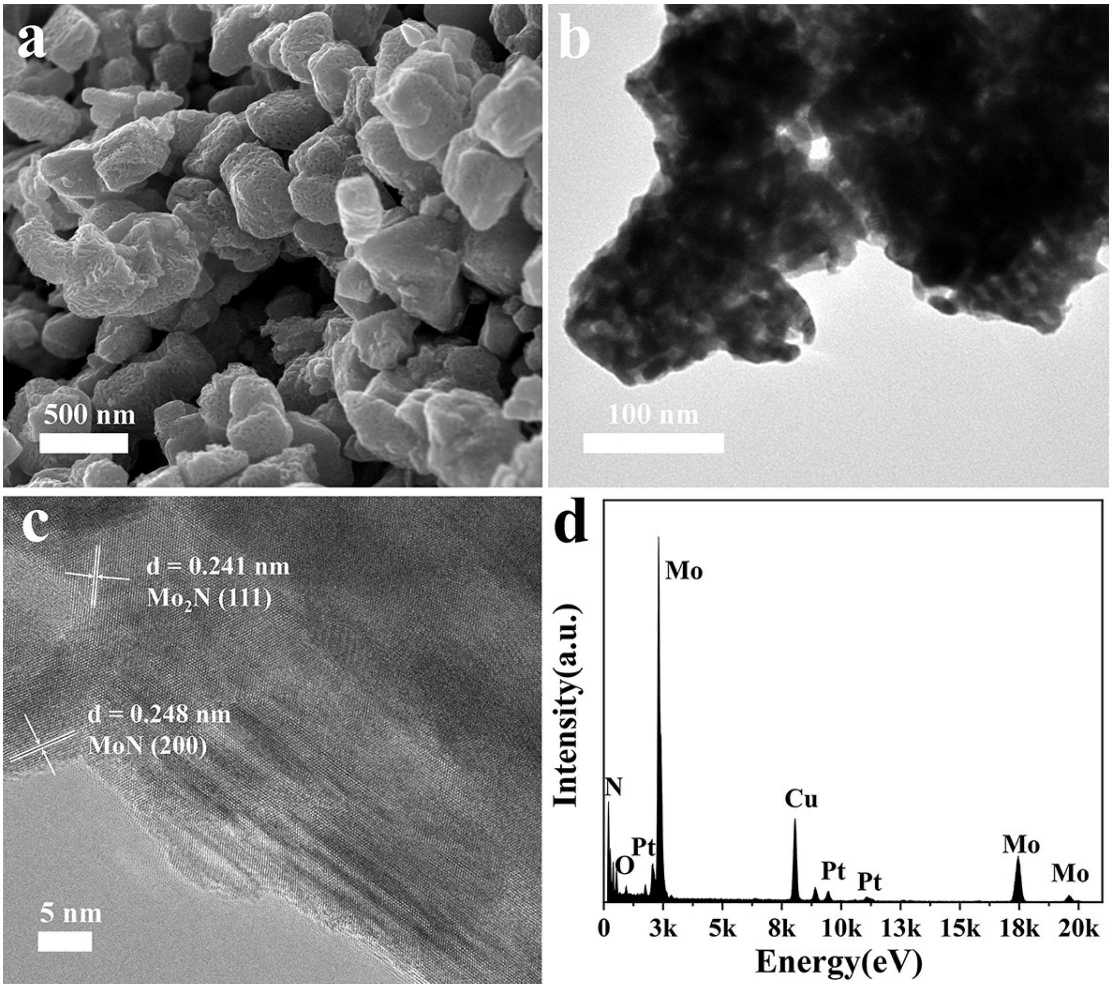

Fig.S3. SEM (a), TEM (b), HRTEM (c), of $MoN_x$; TEM EDX spectrum (d) of Pt-5.

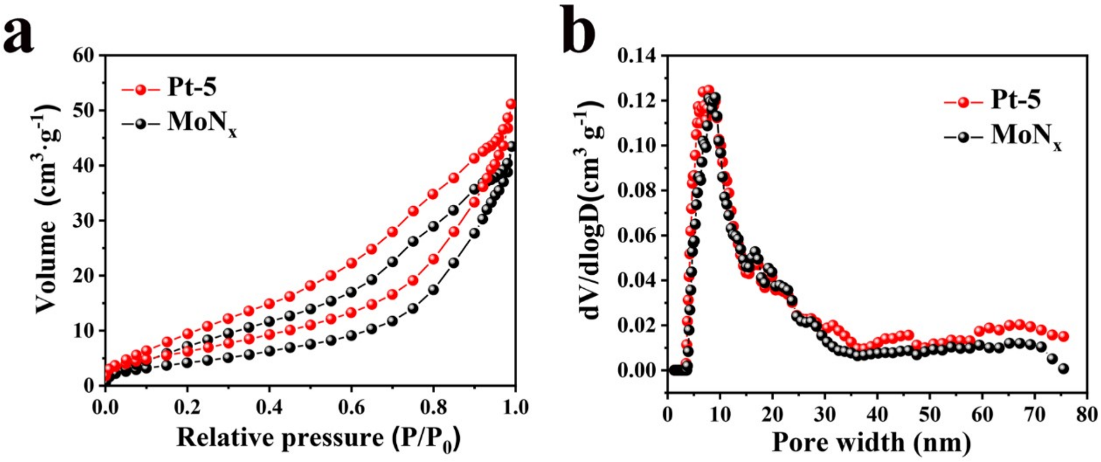

Fig.S4. $N_2$-physisorption isotherms (a) and BJH pore size distribution (b) of Pt-5 and $MoN_x$

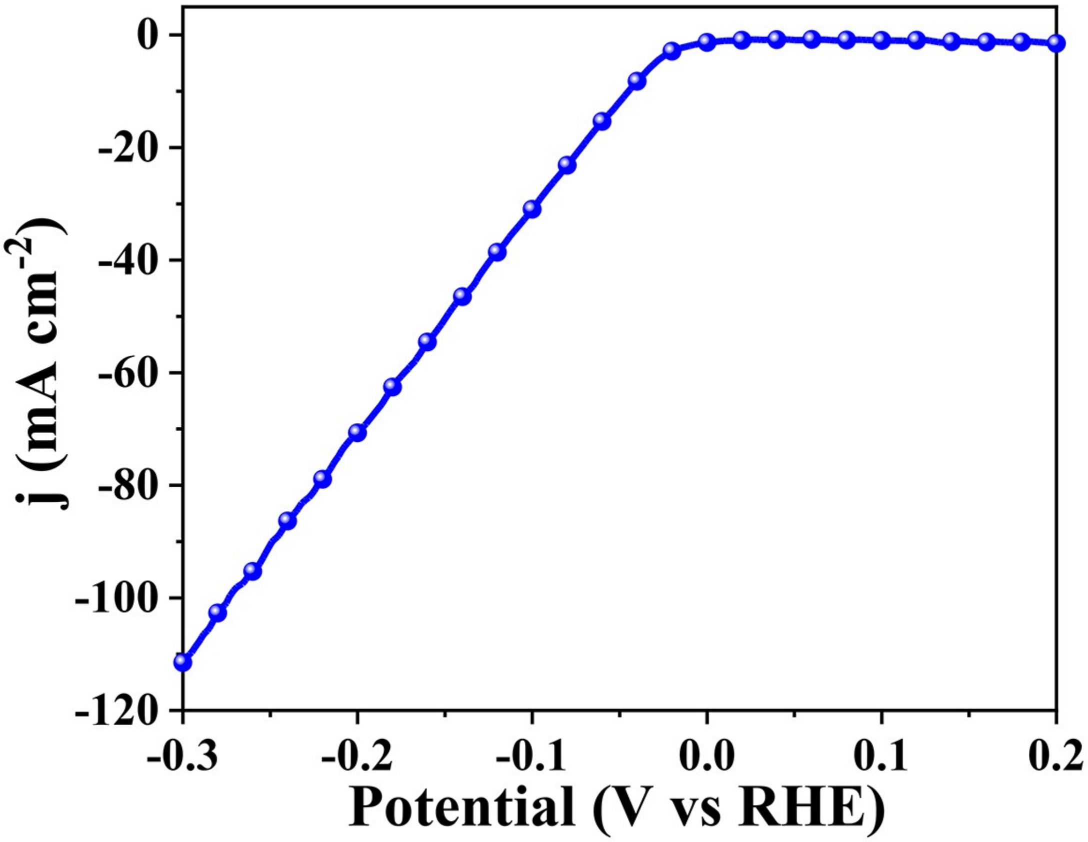

Fig.S5 Polarization curves of Pt-7

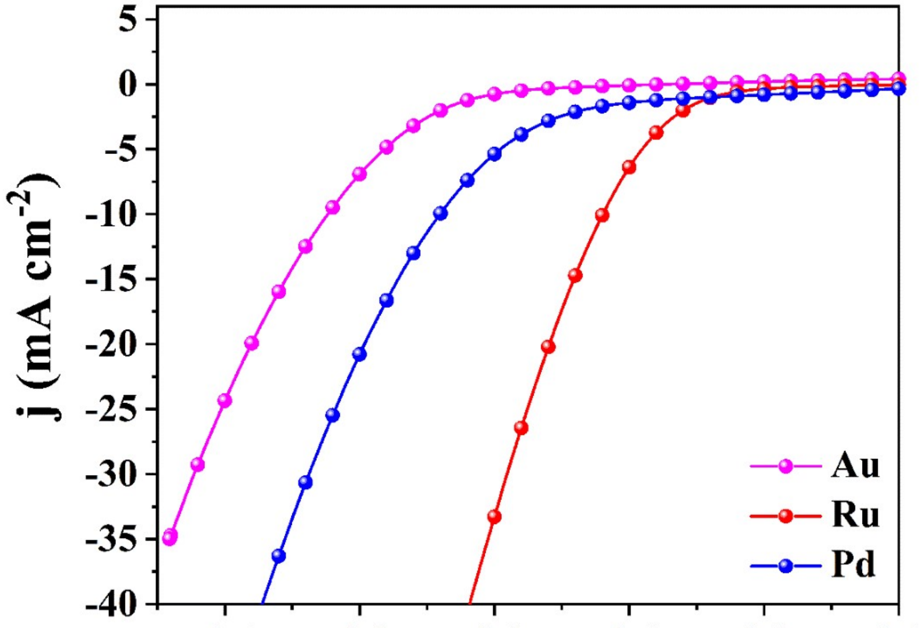

Fig.S6 Polarization curves of Au, Ru, and Pd.

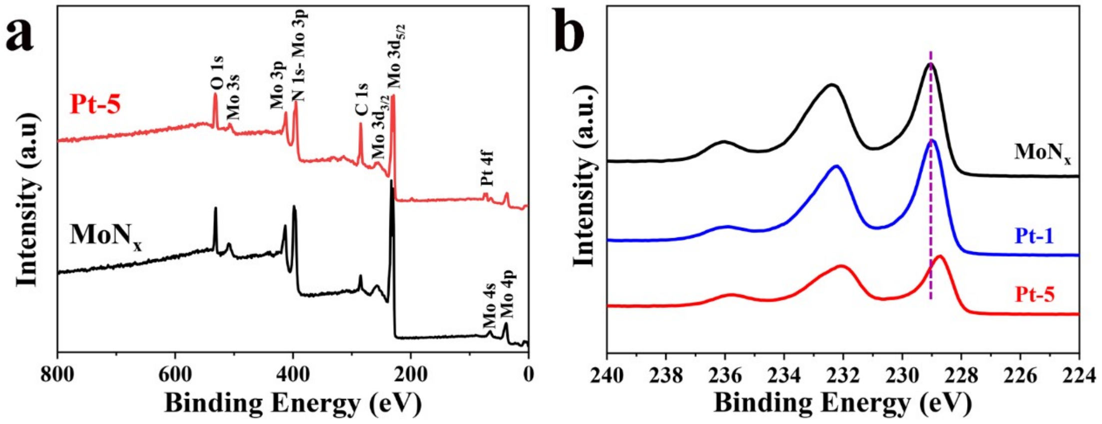

Fig.S7 XPS spectra of catalysts. XPS survey spectrum (a); Mo 3d (b).

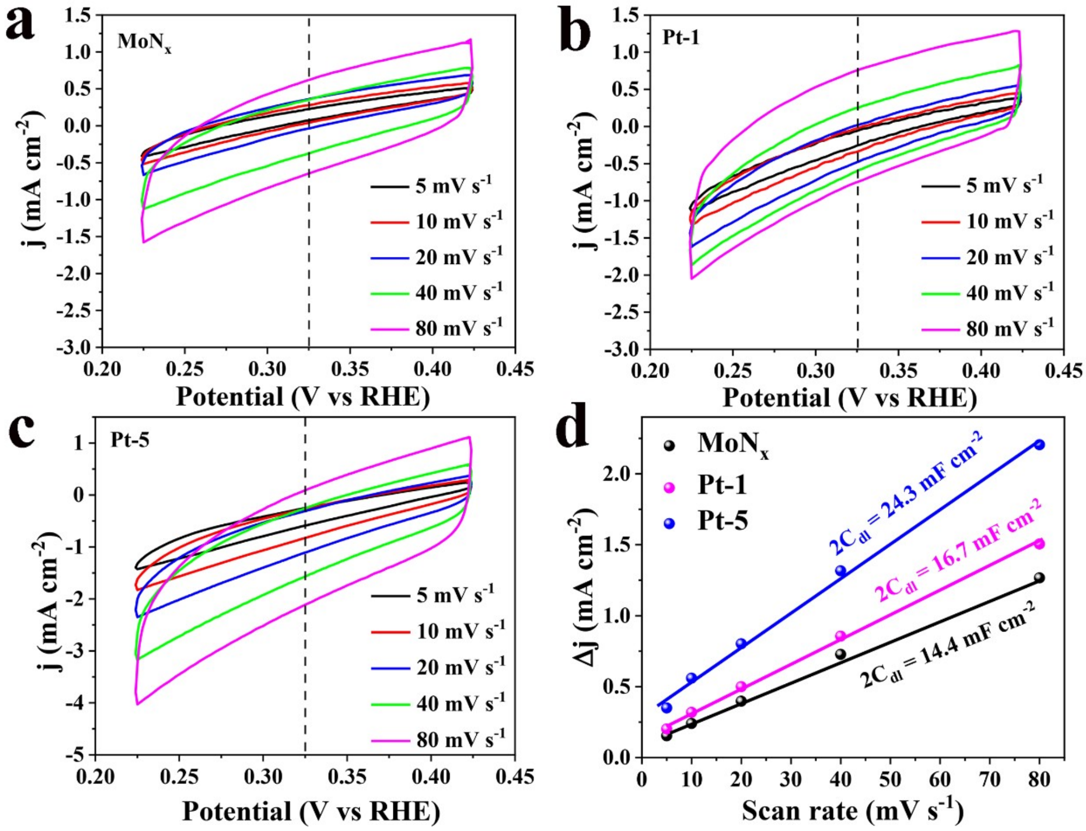

Fig.S8 CV with different rates in the region of 0.224-0.424 V versus RHE for MoN$_x$(a), Pt-1 (b), Pt-5 (c). Electrochemical double–layer capacitance (d).

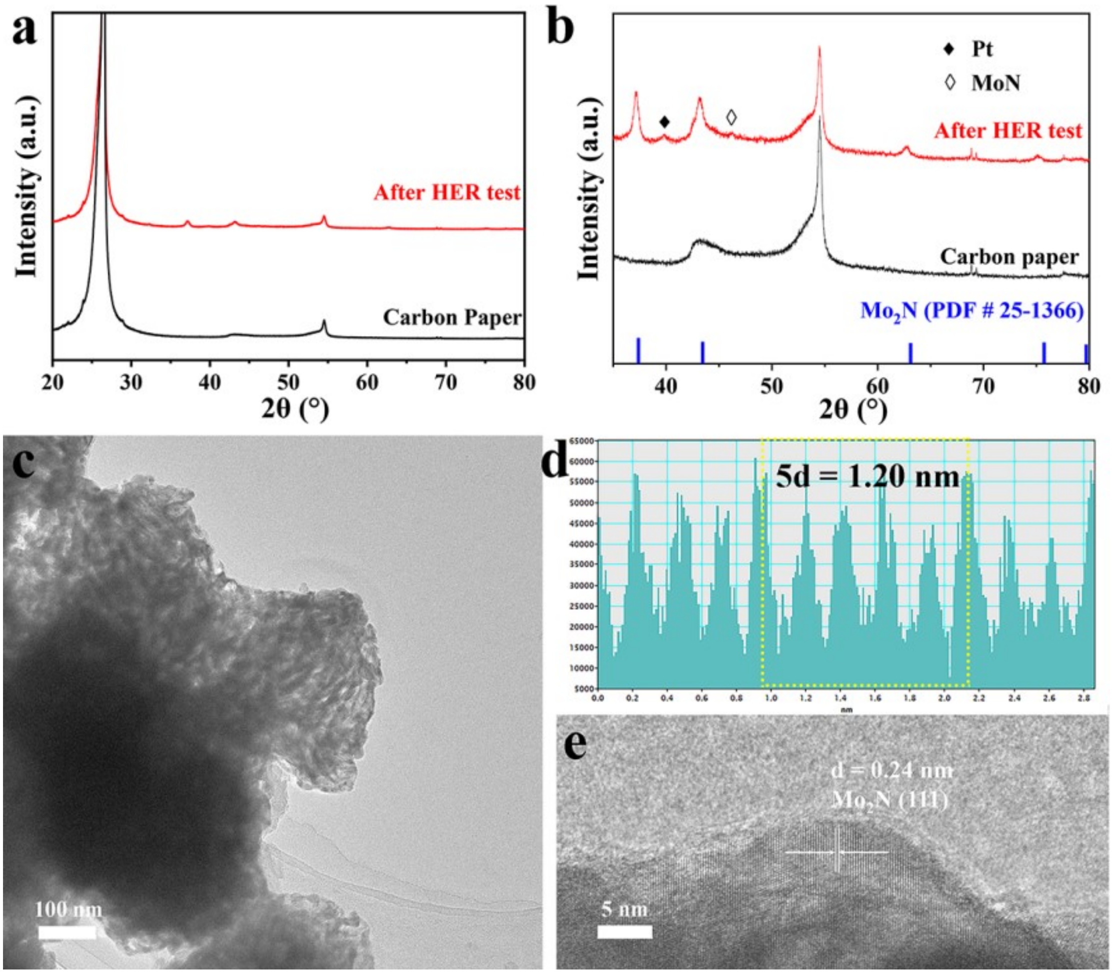

Fig.S9 Post-HER testing characterization of Pt–5. XRD (a and b), HRTEM (c and e), Fourier transformation (FFT) pattern (d).

Table S1 The comparison of HER performance of Pt-5 with other Mo-based electrocatalysts in acidic electrolytes.

| **Catalysts** | **$\eta_{10}$ (mV)** | **Durability** | **Tafel slope (mV dec$^{-1}$)** | **Reference** |
|---|---|---|---|---|
| Pt-SA/α-$MoO_X$ | 19 | 5000 cycles/20 h | 123 | 2 |
| $Mo_2C$@NC@Pt | 27 | 1000 cycles/10 h | 28 | 3 |
| Pt Cs/$MoO_2$ NSs | 47 | 12h | 32.6 | 4 |
| α-$MoC_{1-x}$/Pt | 30 | 10000 cycles | 31 | 5 |
| v$Mo_xC$ | 130 | 20000 s | | 6 |
| $Co_{50}$-$Mo_2C$-12 | 125 | 3000 cycles/12 h | 70.9 | 7 |
| $Mo_xC$ | 155 | 30 h | 48 | 8 |
| $Mo_2C$-$Mo_3C_2$ | 134 | 5000 cycles/13 h | 64 | 9 |
| MoNCs | 157 | 1000 cycles/10 h | 60.6 | 10 |
| $Mo_2C$/G | 175 | 10 h | 88 | 11 |
| h-MoN@BNCNT | 78 | 10000 cycles/24 h | 46 | 12 |
| MoN@NPCNCs | 72 | 3000 cycles | 53 | 13 |
| $Mo_2C$ nanobelts | 140 | 1000 cycles | 51.3 | 14 |
| N,P-MoxC NF | 107 | 1000 cycles | 65.1 | 15 |
| N@MoPCx | 108 | - | 69.4 | 16 |
| $Mo_2N$-$Mo_2C$/Gr-3 | 157 | 2000 cycles/50 h | 55 | 17 |
| MoN-NC | 62 | 3000 cycles/15 h | 54 | 18 |
| dr-MoN | 125 | 20 h | 51 | 19 |
| $Mo_2C$-$MoO_x$/CC$^a$ | 74 | 5000 cycles | 56 | 20 |
| **Pt-5** | **47** | **2000 cycles/ 25h** | **43** | **Our work** |

a 1.0 M $HClO_4$

Table S2 Mo 3d binding energies of samples

| Catalysts | $Mo^{\sigma+}$ (eV) | | $Mo^{4+}$ (eV) | | $Mo^{6+}$ (eV) | |
|---|---|---|---|---|---|---|
| | $3d_{5/2}$ | $3d_{3/2}$ | $3d_{5/2}$ | $3d_{3/2}$ | $3d_{5/2}$ | $3d_{3/2}$ |
| $MoN_x$ | 229.04 | 232.19 | 230.08 | 233.23 | 232.82 | 235.97 |
| Pt-1 | 228.96 | 232.11 | 229.88 | 233.03 | 232.62 | 235.77 |
| Pt-5 | 228.72 | 231.87 | 229.77 | 232.92 | 232.54 | 235.69 |

## References

1 K. Xia, Z. Chen, J. Yi, H. Xu, Y. Yu, X. She, Z. Mo, H. Chen, Y. Xu, H. Li, *Ind. Eng. Chem. Res.* 2018, **57**, 8863-8870.

2 J. Xu, C. Zhang, H. Liu, J. Sun, R. Xie, Y. Qiu, F. Lü, Y. Liu, L. Zhuo, X. Liu, J. Luo, *Nano Energy* 2020, **70**, 104529.

3 J.-Q. Chi, J.-Y. Xie, W.-W. Zhang, B. Dong, J.-F. Qin, X.-Y. Zhang, J.-H. Lin, Y.-M. Chai, C.-G.

Liu, *ACS Appl. Mater. Interfaces* 2019, **11**, 4047-4056.

4 X. Li, J. Yu, J. Jia, A. Wang, L. Zhao, T. Xiong, H. Liu, W. Zhou, *Nano Energy* 2019, **62**, 127-135.

5 H. J. Song, M. C. Sung, H. Yoon, B. Ju, D. W. Kim, *Adv. Sci.* 2019, **6**, 1802135.

6 S. Kim, C. Choi, J. Hwang, J. Park, J. Jeong, H. Jun, S. Lee, S.-K. Kim, J. H. Jang, Y. Jung, J. Lee, *ACS Nano* 2020, **14**, 4988-4999.

7 Y. Ma, M. Chen, H. Geng, H. Dong, P. Wu, X. Li, G. Guan, T. Wang, *Adv. Funct. Mater.* 2020, **30**, 2000561.

8 X. Zhang, J. Wang, T. Guo, T. Liu, Z. Wu, L. Cavallo, Z. Cao, D. Wang, *Appl. Catal. B: Environ.* 2019, **247**, 78-85.

9 L. Jia, C. Li, Y. Zhao, B. Liu, s. cao, D. Mu, T. Han, G. Chen, Y. Lin, *Nanoscale* 2019, **11**, 23318-23329.

10 C. Lei, W. Zhou, Q. Feng, Y. Lei, Y. Zhang, Y. Chen, J. Qin, *Nano-Micro Lett.* 2019, **11**, 45.

11 H. Huang, C. Yu, H. Huang, W. Guo, M. Zhang, X. Han, Q. Wei, S. Cui, X. Tan, J. Qiu, *Small Methods* 2019, **3**, 1900259.

12 J. Miao, Z. Lang, X. Zhang, W. Kong, O. Peng, Y. Yang, S. Wang, J. Cheng, T. He, A. Amini, Q. Wu, Z. Zheng, Z. Tang, C. Cheng, *Adv. Funct. Mater.* 2019, **29**, 1805893.

13 M.-Q. Wang, C. Tang, C. Ye, J. Duan, C. Li, Y. Chen, S.-J. Bao, M. Xu, *J. Mater. Chem. A* 2018, **6**, 14734-14741.

14 S. Jing, L. Zhang, L. Luo, J. Lu, S. Yin, P. K. Shen, P. Tsiakaras, *Appl. Catal. B: Environ.* 2018, **224**, 533-540.

15 L. Ji, J. Wang, X. Teng, H. Dong, X. He, Z. Chen, *ACS Appl. Mater. Interfaces* 2018, **10**, 14632-14640.

16 Y. Huang, J. Ge, J. Hu, J. Zhang, J. Hao, Y. Wei, *Adv. Energy Mater.* 2018, **8**, 1701601.

17 H. Yan, Y. Xie, Y. Jiao, A. Wu, C. Tian, X. Zhang, L. Wang, H. Fu, *Adv. Mater.* 2018, **30**, 1704156.

18 Y. Zhu, G. Chen, X. Xu, G. Yang, M. Liu, Z. Shao, *ACS Catal.* 2017, **7**, 3540-3547.

19 J. Xiong, W. Cai, W. Shi, X. Zhang, J. Li, Z. Yang, L. Feng, H. Cheng, *J. Mater. Chem. A* 2017, **5**, 24193-24198.

20 L. He, W. Zhang, Q. Mo, W. Huang, L. Yang, Q. Gao, *Angew. Chem. Int. Ed.* 2020, **59**, 3544-3548.