

## Supporting Information

### **Ultralow-Loading Pt Single Atoms Anchored on N-Doped Carbon-Encapsulated Mo<sub>2</sub>C Microspheres for Efficient Hydrogen Evolution**

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Yaqiang Li<sup>c,\*</sup>, Zailai Xie<sup>b,c,\*</sup>, and Xuefei Zhang<sup>a,\*</sup>

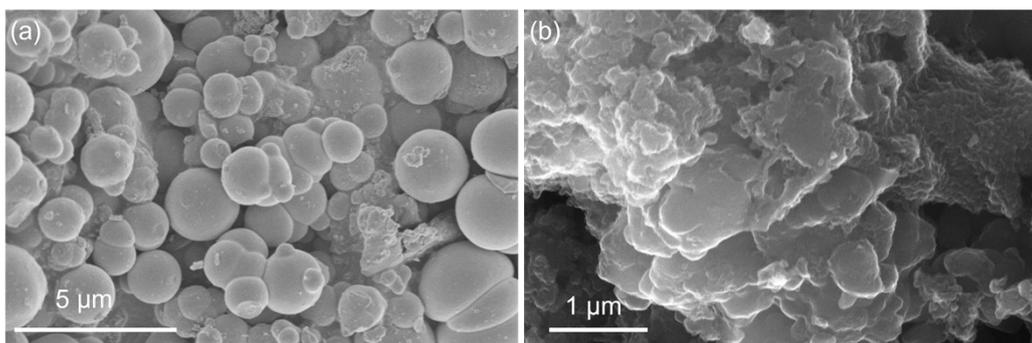
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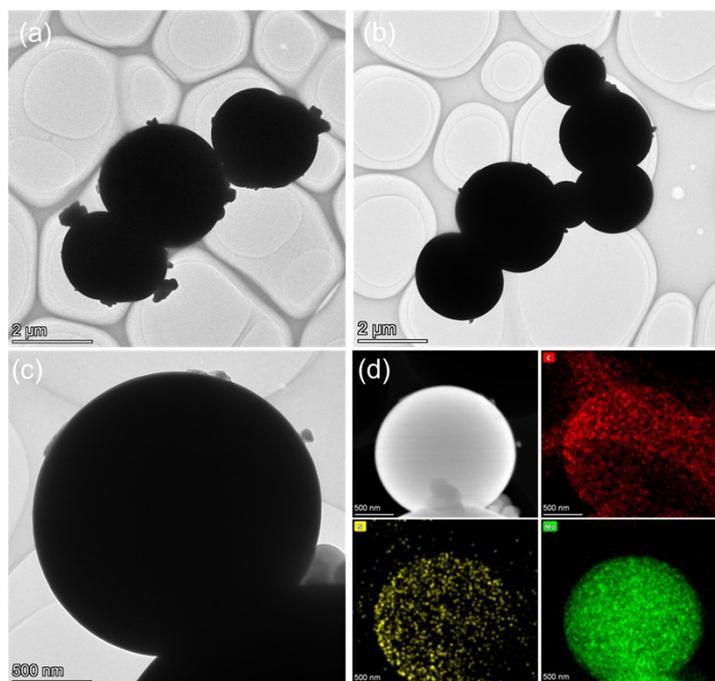
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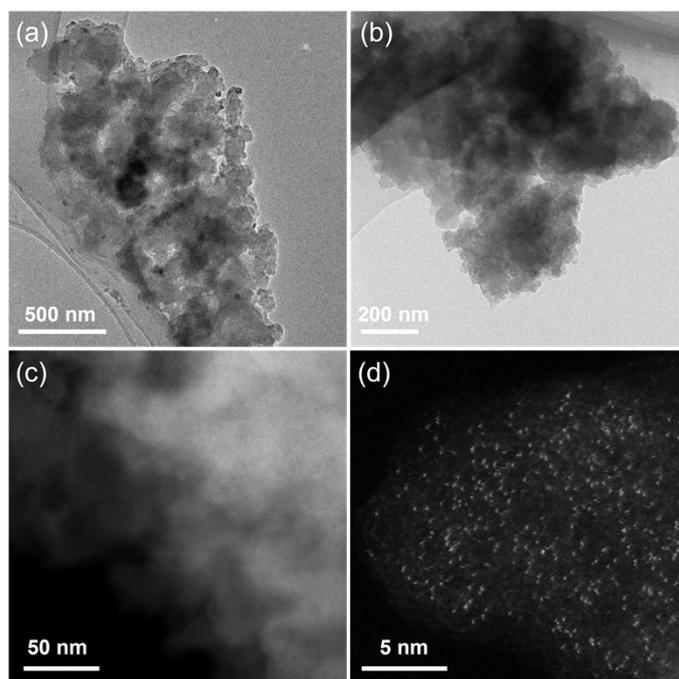
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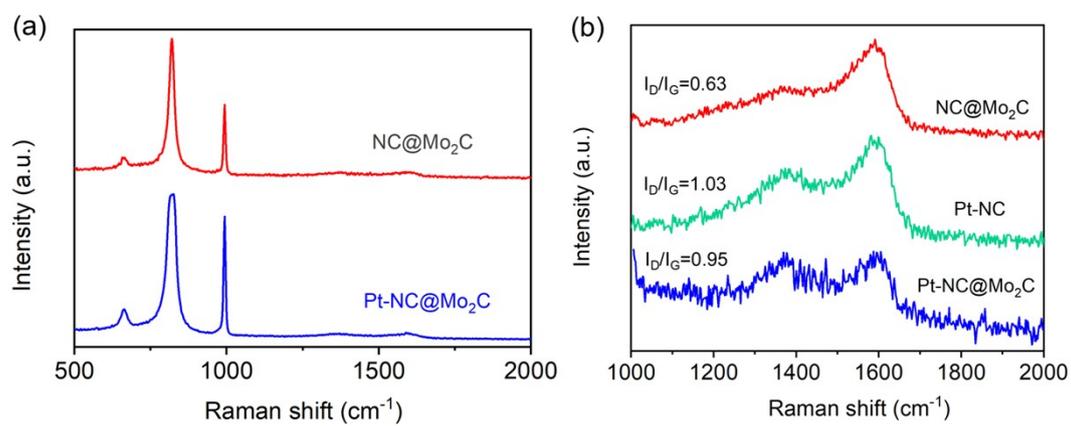
**Fig. S1.** (a) SEM images of NC@Mo<sub>2</sub>C. (b) SEM images of Pt-NC sample.



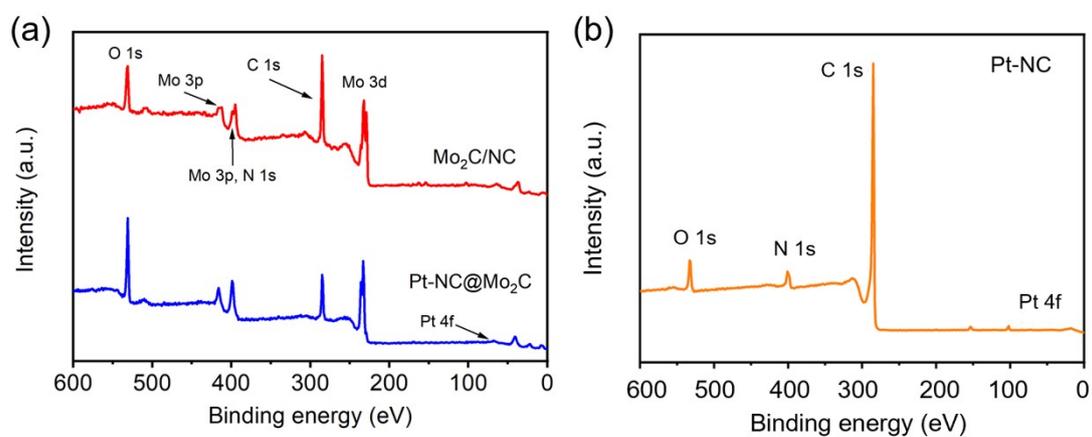
**Fig. S2.** (a-c) TEM images. (d) HAADF-STEM and corresponding EDX elemental mapping images of NC@Mo<sub>2</sub>C.



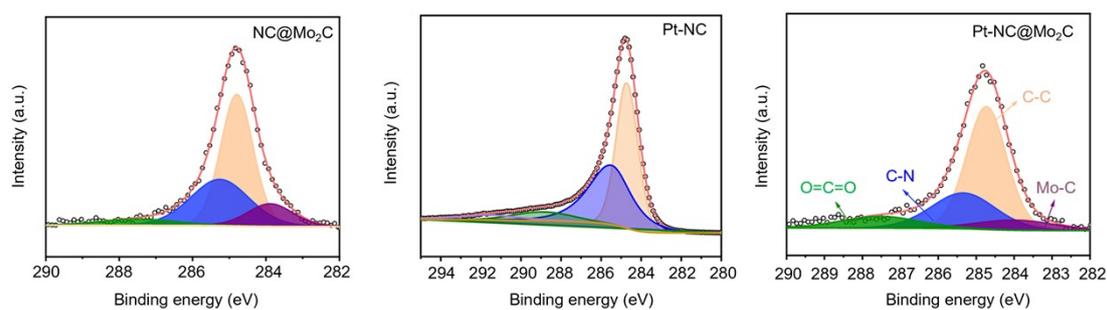
**Fig. S3.** (a, b) TEM images. (c,d) AC-STEM images of Pt-NC.



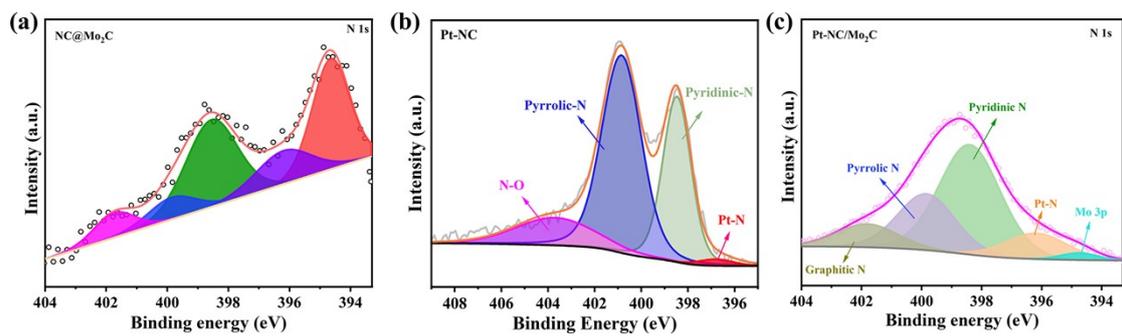
**Fig. S4.** (a) Raman spectra Pt-NC@Mo<sub>2</sub>C and NC@Mo<sub>2</sub>C. (b) Magnified Raman spectra of Pt-NC, Pt-NC@Mo<sub>2</sub>C, and NC@Mo<sub>2</sub>C samples.



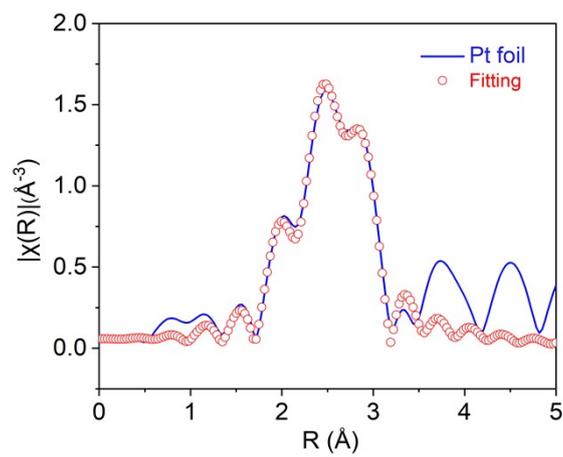
**Fig. S5.** (a) Survey of  $\text{NC}@Mo_2\text{C}$  and  $\text{Pt-NC}@Mo_2\text{C}$ . (b) Survey of Pt-NC sample.



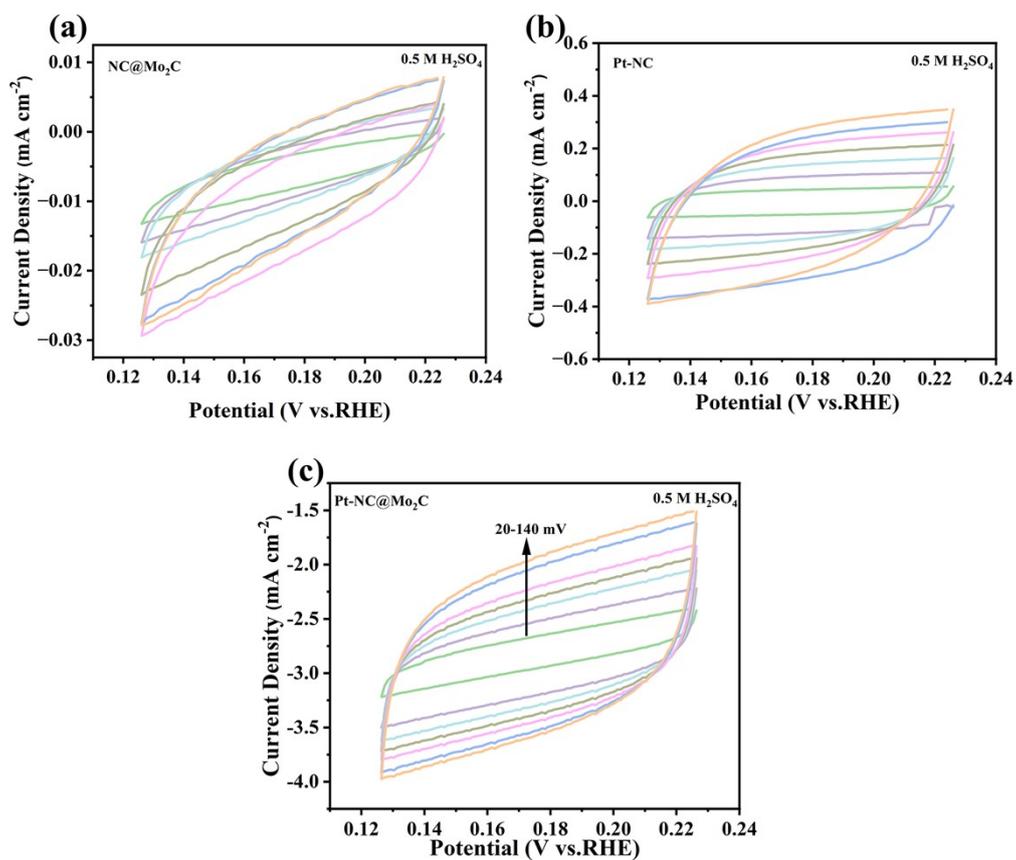
**Fig. S6.**  $\text{C } 1s$  XPS spectra of  $\text{NC}@Mo_2\text{C}$ , Pt-NC, and  $\text{Pt-NC}@Mo_2\text{C}$  samples.



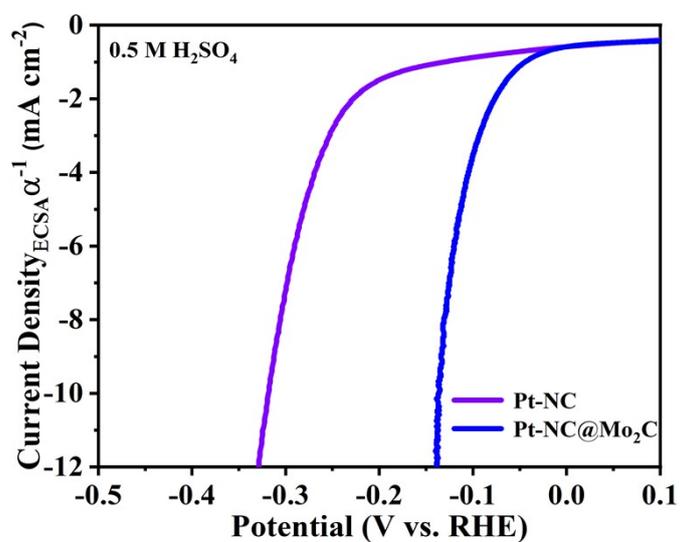
**Fig. S7.** N 1s XPS spectra of NC@Mo<sub>2</sub>C, Pt-NC, and Pt-NC@Mo<sub>2</sub>C samples.



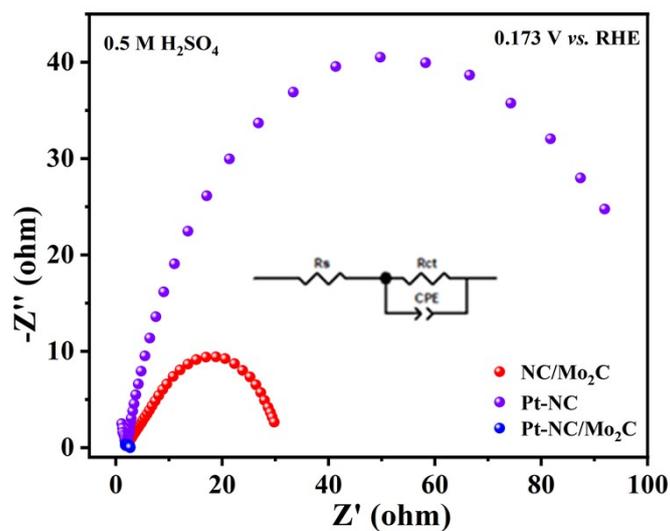
**Fig. S8.** Corresponding EXAFS fitting curve in  $R$  space of Pt foil.



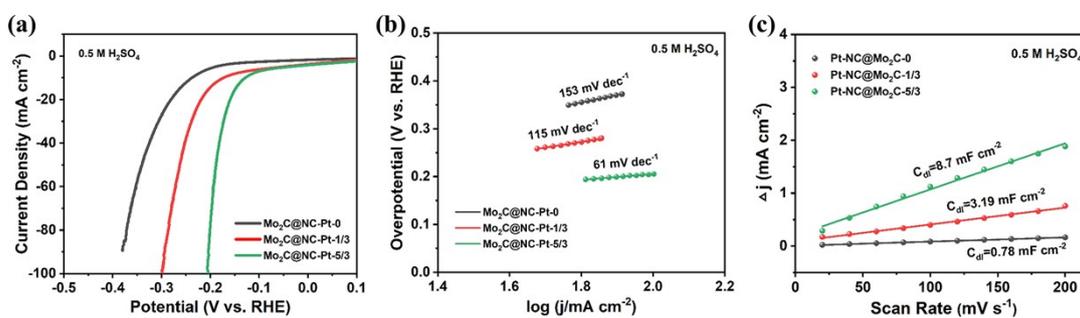
**Fig. S9.** CV curves of (a) NC@Mo<sub>2</sub>C, (b) Pt-NC and (c) Pt-NC@Mo<sub>2</sub>C at different scan rates in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



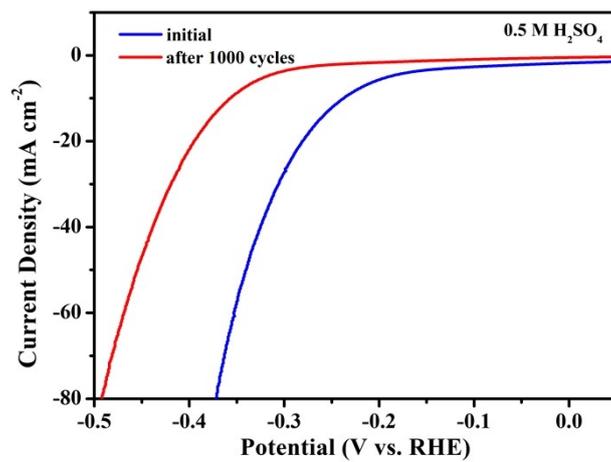
**Fig. S10.** ECSA-normalized LSV curves of Pt-NC and Pt-NC@Mo<sub>2</sub>C in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



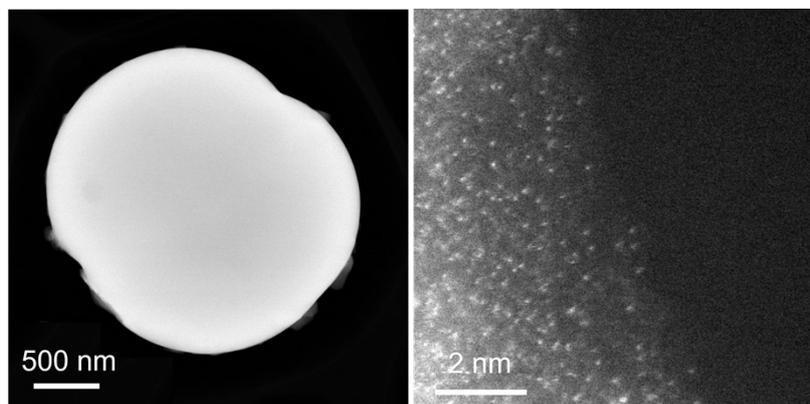
**Fig. S11.** EIS Nyquist plots of different catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



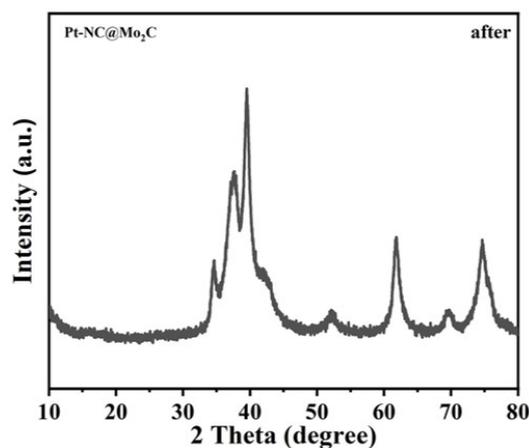
**Fig. S12.** (a) Polarization curves. (b) Tafel plots and (c) Capacitive  $\Delta j$  ( $= j_a - j_c$ ) against scan rates of in 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous media on Pt-NC@Mo<sub>2</sub>C-0, Pt-NC@Mo<sub>2</sub>C-1/3, and Pt-NC@Mo<sub>2</sub>C-5/3.



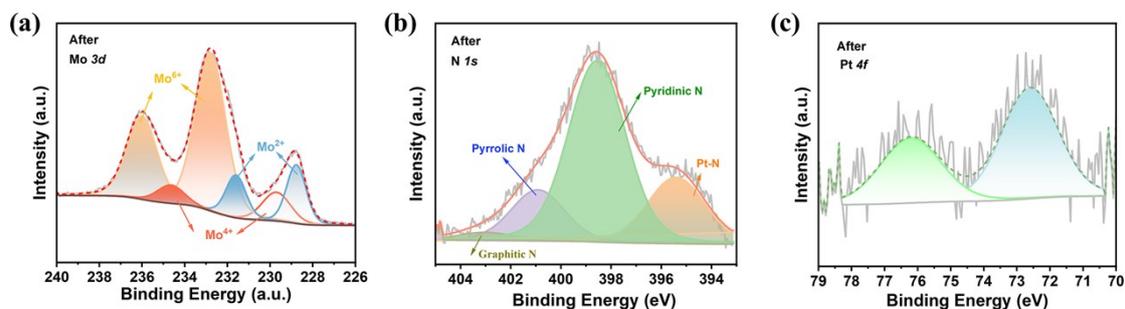
**Fig. S13.** LSV curves of Pt-NC before and after 1000 cycles in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



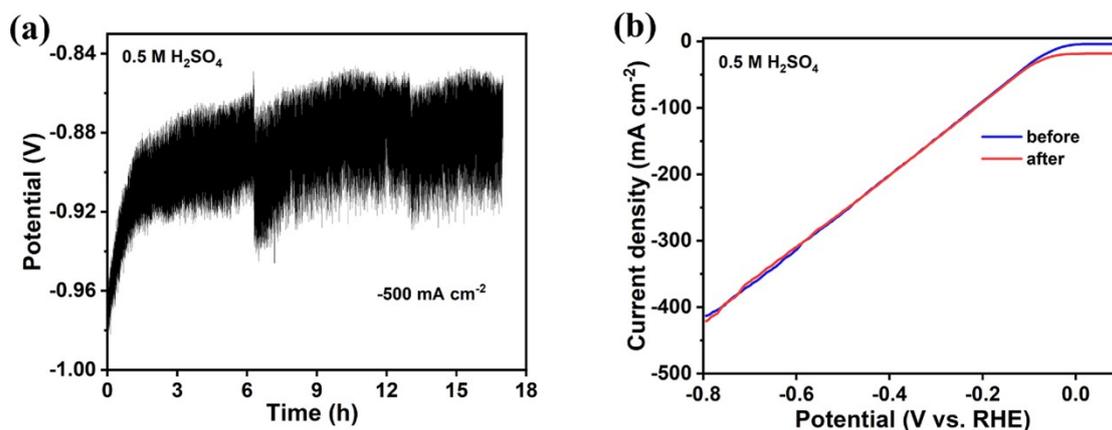
**Fig. S14.** AC-STEM images of Pt-NC@Mo<sub>2</sub>C after long-time stability test in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



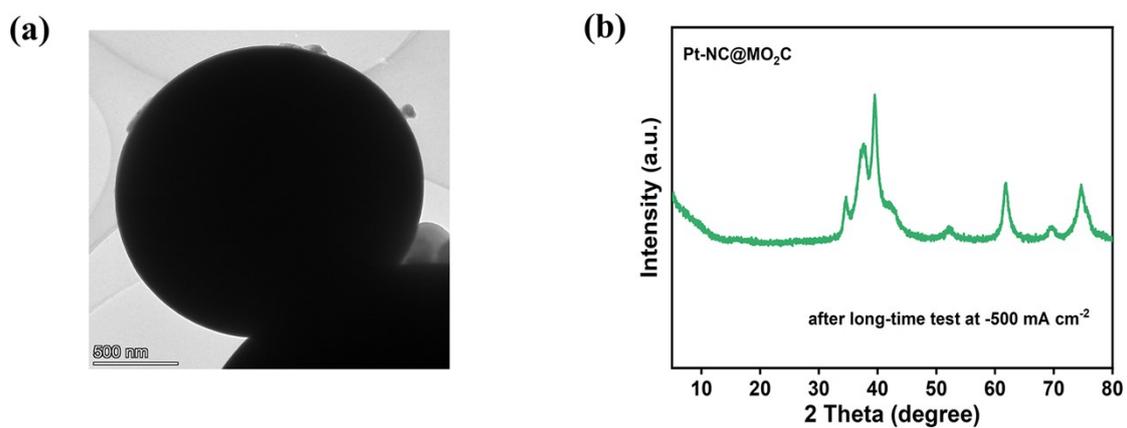
**Fig. S15.** XRD pattern of Pt-NC@Mo<sub>2</sub>C after long-time stability test in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



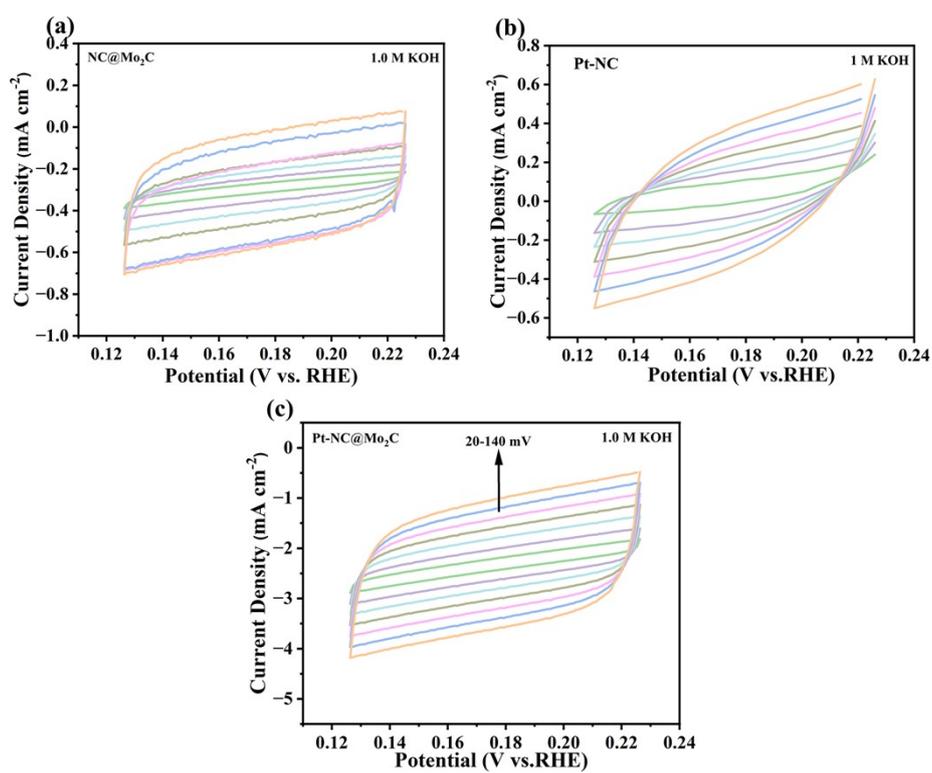
**Fig. S16.** XPS patterns of Pt-NC@Mo<sub>2</sub>C after long-time stability test in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



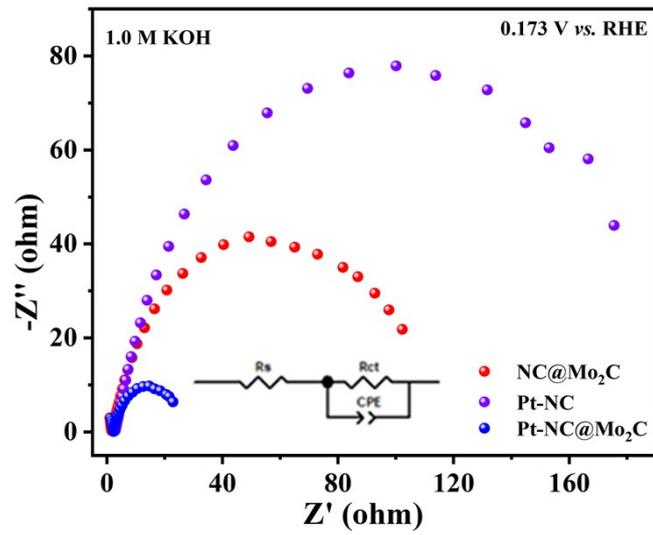
**Fig. S17.** (a) Long-term stability test of Pt-NC@Mo<sub>2</sub>C under -500 mA cm<sup>-2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> and (b) LSV curves of before and after long-term stability test in a H-cell system.



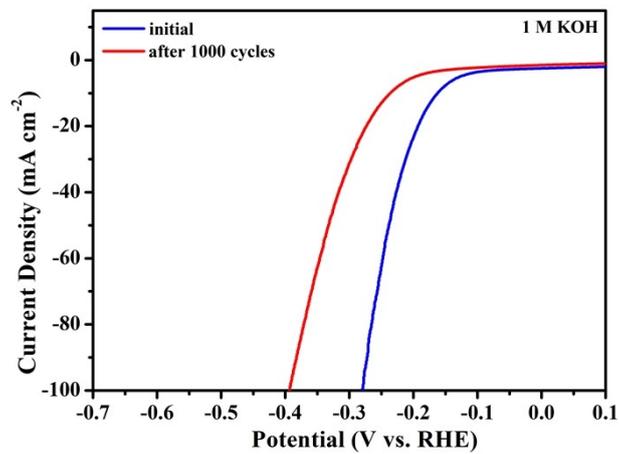
**Fig. S18.** (a) TEM and (b) XRD pattern of Pt-NC@Mo<sub>2</sub>C after 15 h stability test under -500 mA cm<sup>-2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



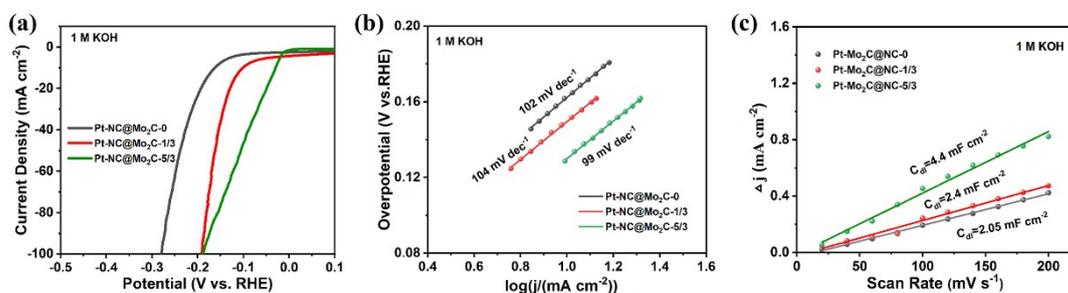
**Fig. S19.** CV curves of (a) NC@Mo<sub>2</sub>C, (b) Pt-NC and (c) Pt-NC@Mo<sub>2</sub>C at different scan rates in 1.0 M KOH.



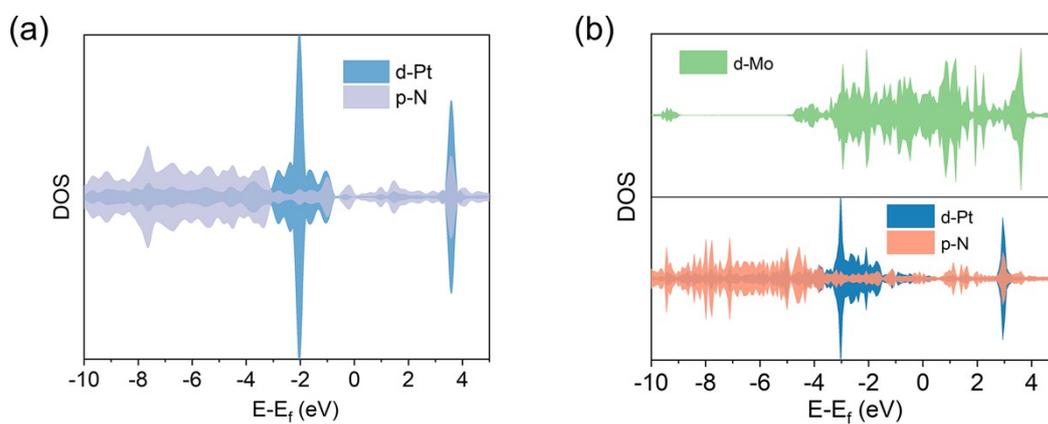
**Fig. S20.** EIS Nyquist plots of different catalysts in 1.0 M KOH.



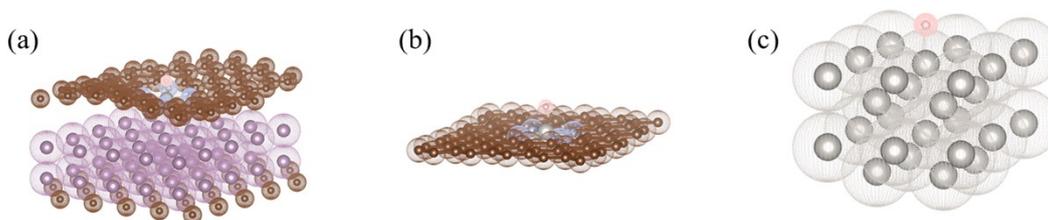
**Fig. S21.** LSV curves of Pt-NC before and after 1000 cycles in 1.0 M KOH.



**Fig. S22.** (a) Polarization curves. (b) Tafel plots and (c) Capacitive  $\Delta j$  ( $= j_a - j_c$ ) against scan rates of in 1 M KOH aqueous media on Pt-NC@Mo<sub>2</sub>C-0, Pt-NC@Mo<sub>2</sub>C-1/3, and Pt-NC@Mo<sub>2</sub>C-5/3.



**Fig. S23.** DOS for PtN<sub>4</sub> and PtN<sub>4</sub>/Mo<sub>2</sub>C obtained by spin-polarization DFT calculation.



**Fig. S24.** (a-c) adsorption configuration of H\* on Pt-NC@Mo<sub>2</sub>C, Pt-NC and Pt.

**Table S1.** Structural parameters of Pt L<sub>3</sub>-edge were extracted from EXAFS fitting.

Sample	Path	CN	R(Å)	$\sigma^2(10^{-3}\text{Å}^2)$	$\Delta E_0$ (eV)	R-factor
Pt foil	Pt-Pt	12*	2.76±0.05	4.5±0.4	7.0±0.5	0.0064
Pt-NC@Mo <sub>2</sub> C	Pt-N/C	4.2±0.3	1.97±0.03	3.5±1.0	6.8±1.4	0.0025

CN, coordination number;  $R$ , the distance to the neighboring atom;  $\sigma^2$ , Debye-Waller factors;

$\Delta E_0$ , inner potential correction; The  $R$ -factor indicates the goodness of the fit.

$S_0^2$  was fixed at 0.80 based on the experimental EXAFS fitting results for Pt foil, respectively.

Fitting range:  $3.0 \leq k (\text{Å}^{-1}) \leq 12$  and  $1.0 \leq R (\text{Å}) \leq 3.2$  (Pt foil).

$3.0 \leq k (\text{Å}^{-1}) \leq 12$  and  $1.15 \leq R (\text{Å}) \leq 2$  (Pt-NC@Mo<sub>2</sub>C).

$3.0 \leq k (\text{Å}^{-1}) \leq 10$  and  $1.0 \leq R (\text{Å}) \leq 3.0$  (Fe/Co-CN).

A reasonable range of EXAFS fitting parameters:  $0.700 < S_0^2 < 1.000$ ;  $CN > 0$ ;  $\sigma^2 > 0 \text{ Å}^2$ ;  $|\Delta E_0| < 10 \text{ eV}$ ;  $R\text{-factor} < 0.02$ .

**Table S2.** Comparison of the HER performance of Pt-NC@Mo<sub>2</sub>C with reported Pt-based catalysts.

Electrocatalysts	<i>j</i> (mA cm <sup>-2</sup> )	<i>η</i> (mV)	Tafel slop (mV dec <sup>-1</sup> )	Electrolyte	Ref.
<b>Pt-NC@Mo<sub>2</sub>C</b>	<b>10</b>	<b>37</b>	<b>60.94</b>	<b>0.5 M H<sub>2</sub>SO<sub>4</sub></b>	<b>This Work</b>
	<b>10</b>	<b>100</b>	<b>81.53</b>	<b>1.0 M KOH</b>	
20 % Pt/C	10	47	54.35	0.5 M H <sub>2</sub> SO <sub>4</sub>	
	10	15	43.24	1.0 M KOH	
Pt(Mo <sub>2</sub> C)	10	75	-	0.5 M H <sub>2</sub> SO <sub>4</sub>	1
Pt (5wt%)-MoNx	10	47	57	0.5 M H <sub>2</sub> SO <sub>4</sub>	2
Pt/Mo <sub>2</sub> C-HCNFs	10	27	55.15	0.5 M H <sub>2</sub> SO <sub>4</sub>	3
	10	41	100.13	1.0 M KOH	
Mo <sub>2</sub> C@NC@Pt	10	27	28	0.5 M H <sub>2</sub> SO <sub>4</sub>	4
	10	47	57	1.0 M KOH	
CoFeLDH-Pt <sub>40cls</sub>	10	45	70	1.0 M KOH	5
Pt/Mo <sub>2</sub> C (C)	10	38	24	0.5 M H <sub>2</sub> SO <sub>4</sub>	6
Pt <sub>1</sub> -Mo <sub>2</sub> C-C	10	155	64	1.0 M KOH	7
PtSA@Mo <sub>2</sub> @NC	10	26	-	0.5 M H <sub>2</sub> SO <sub>4</sub>	8
Pt-N-CoO	10	22	33	0.5 M H <sub>2</sub> SO <sub>4</sub>	9
Pt <sub>SA</sub> Pt <sub>NC</sub> -CeO <sub>2</sub> /N-rGO	10	26	18.3	1.0 M KOH	10

**Table S3.** Elements content analysis of fresh and spent Pt-NC@Mo<sub>2</sub>C catalysts.

Sample	C (at, %)	N (at, %)	O (at, %)	Mo (at, %)	Pt (at, %)
Pt-NC@Mo <sub>2</sub> C	59.31	11.86	19.27	9.37	0.19
Pt-NC@Mo <sub>2</sub> C-used	52.59	19.63	19.03	8.64	0.11

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