

## Electronic Supplementary Information (ESI)

# Mo<sub>2</sub>C promoted electrocatalysis of Pt/Mo<sub>2</sub>C (C) heterostructure for superior hydrogen evolution reaction

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## 2. Experimental section

### 2.1. Materials

Vulcan-C was obtained from Cabot Corporation (USA). Commercial Pt/C (20%) catalyst was purchased from Johnson-Matthey. 5% Nafion 117 solution was supplied by Sigma-Aldrich.  $\text{H}_2\text{SO}_4$ ,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ,  $\text{K}_2\text{PtCl}_4$ , Cetyltrimethylammonium bromide (CTAB) and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), and all the chemicals were of analytical grade. The resistance of deionized water (DI) was 18.25 M $\Omega$ .

### 2.2. Characterization

Sample composition was identified from its X-ray diffraction patterns obtained on a X'pert Pro (PANaly, Holland) using filtered Cu-K $\alpha$  radiation source (40 kV, 40 mA). Data were collected in the range of 5-90° at a scanning rate of 0.15 deg·min<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) was conducted on a VG ESCALAB250 spectrometer (Thermo Scientific, USA) with Al-K $\alpha$  radiation (1486.6 eV). The method of energy calibration is a charged correction, using 284.6 eV as standard value to calibrate C1s spectra. According to the difference of C1s spectra, then all the XPS spectra of the remaining elements increase or decrease to a certain value. Then the software "XPSPEAK (Version 4.1)" was used to analyze data, and the steps include importing data, establishing baseline, adding peak (according to references and relevant rules), and adjusting parameters (FWHM 0.5-3.5eV, the area of peak, etc.). The morphology and microstructures of the as-synthesized catalysts were characterized using scanning electron microscope (SEM, JSM-7500F, JEOL Ltd.,

Japan). TEM, HRTEM, HAAD-FSTEM and elemental distribution mapping were performed on an FEI Tecnai G2 F20 transmission electron microscope. The Pt content in the catalysts was measured by Inductively coupled plasma-atomic emission spectroscopy (ICP-AES, ICAP6300, Thermo Scientific, USA).

### 2.3. Electrochemical Measurements

The working electrode was modified as follows: 2 mg of catalysts in a mixture of 100  $\mu\text{L}$  5 wt% Nafion solution and 900  $\mu\text{L}$  ethanol was dispersed under ultrasonication for about 60 min to generate a homogeneous catalyst ink. Then, 20  $\mu\text{L}$  of the dispersed liquid was dropped on the rotating ring disk electrode or carbon paper fixed by electrode clamp, and dried naturally for use. All electrochemical measurements were performed in 0.5 M  $\text{H}_2\text{SO}_4$  aqueous solution purged with  $\text{N}_2$  for 40 min at room temperature. Linear sweep voltammetry (LSV) polarization curve was collected at a sweep speed of  $5 \text{ mV s}^{-1}$  with a rotation speed of 1600 rpm. The Tafel plots for studying the HER mechanism were acquired by transforming the corresponding LSV curves. Electrochemical impedance spectroscopy (EIS) measurements were conducted in a frequency range of 0.01 Hz to  $10^5$  Hz, with an amplitude of 5 mV at a fixed voltage of -0.04 V (vs. RHE). Stability was obtained by continuous cyclic voltammetry tests in the potential range from 0.141 to -0.309 V vs. RHE for 1000 cycles at a scan rate of  $50 \text{ mV s}^{-1}$ . Chronopotentiometry tests were measured at the constant current density of  $10 \text{ mA cm}^{-2}$ . The actual amount of  $\text{H}_2$  production was obtained through on-line real-time testing of gas chromatograph. All the potentials in this work were calibrated to the reversible hydrogen electrode (RHE)

according to the formula <sup>1-3</sup>:  $E(\text{RHE}) = E(\text{SCE}) + 241 \text{ mV} + (59 \text{ mV}) \text{ pH}$ .

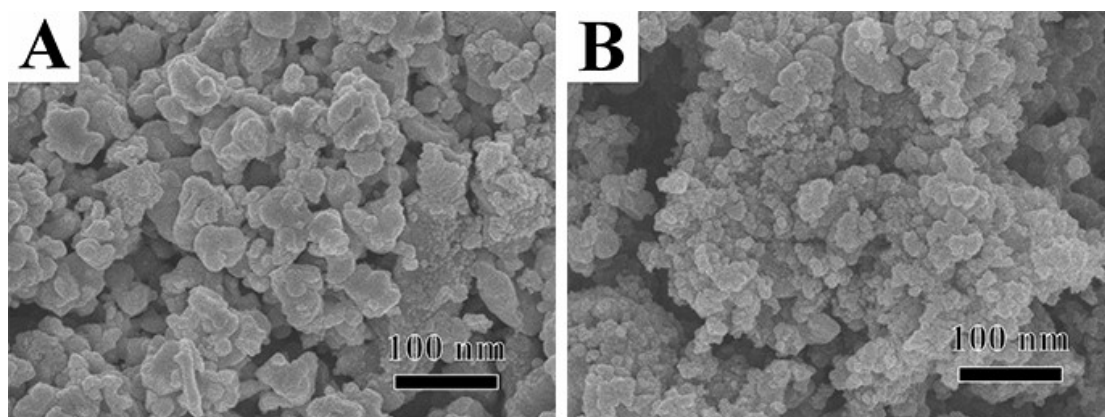


Fig. S1 SEM images: (A) Pt/Mo<sub>2</sub>C, (B) Pt/Mo<sub>2</sub>C (C)

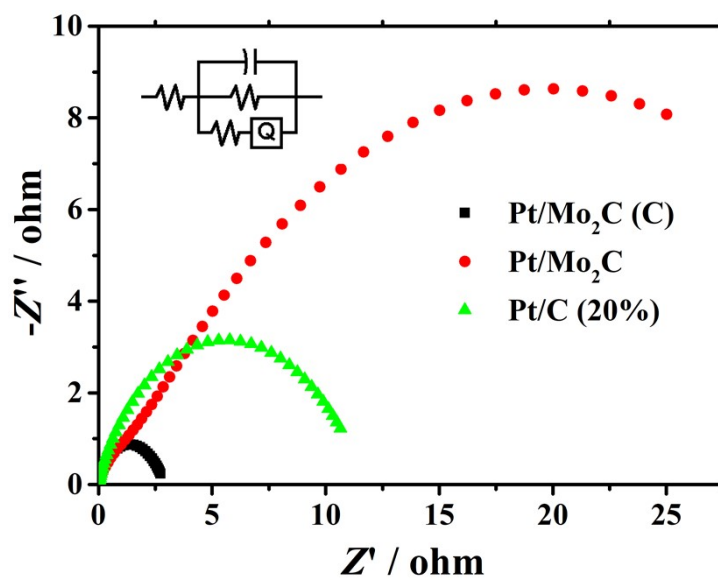


Fig. S2 Nyquist curves of EIS for Pt/Mo<sub>2</sub>C (C), Pt/Mo<sub>2</sub>C, and Pt/C (20%).

**Table S1. The comparison of electrochemical performance with the reported Pt-based catalysts for HER.**

Catalysts	Electrolyte	Pt loading (Wt%)	$\eta_{10}^a$ (mV)	Tafel slope (mV $\square$ dec $^{-1}$ )	Reference s
Pt/Mo <sub>2</sub> C (C)	0.5 M H <sub>2</sub> SO <sub>4</sub>	14.82	38	24	This work
PtCoNi FNs	0.5 M H <sub>2</sub> SO <sub>4</sub>	84.98	41	37	4
Pt-SA-NSFC	0.5 M H <sub>2</sub> SO <sub>4</sub>	15.6	45	65	5
Pt <sub>78</sub> Co <sub>22</sub> NCs/rGO	0.5 M H <sub>2</sub> SO <sub>4</sub>	79.1	25.3	26	6
Pt/SiNW	0.5 M H <sub>2</sub> SO <sub>4</sub>	30.5	220	-	7
Pt <sub>75</sub> Co <sub>25</sub> NDAAs	0.5 M H <sub>2</sub> SO <sub>4</sub>	90.86	34	30	8
Pt-MoS <sub>2</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	36	~50	40	9

<sup>a</sup> The overpotential at the current density of 10 mA cm $^{-2}$

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