

Support Information

for

Designed formation of hollow Pt nanocrystals supported on
MoO_x-modified carbon for high-performance of methanol
electrooxidation

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Number of tables: 2

Note: The figures, tables and text in this Supporting Information document are presented in the order in which they are referenced in the main paper.

Experimental Details

Materials

Sodium chloroplatinic acid (Na_2PtCl_6), silver nitrate (AgNO_3), sodium chloride (NaCl), ammonium hydroxide (NH_4OH , 25 wt%), phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$, HPMo), 1-aminopyrene (AP), sodium borohydride (NaBH_4) and sodium citrate were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Ethylene glycol (EG), methanol, sulfuric acid (H_2SO_4), ethanol and other chemical reagents were purchased from Jiangtian Chemical Technology Co. Ltd., China. Carbon black (Vulcan XC-72), commercial carbon supported Pt-Ru catalyst from Johnson Matthey (PtRu/C-JM, Pt and Ru loadings in this catalyst are 20 % and 10 % in theory, respectively) and Nafion solution (5 wt%) were purchased from Hesen electric Co. Ltd., China. High purity nitrogen ($\geq 99.99\%$) was supplied by Tianjin dongxiang Co. Ltd., China. All aqueous solutions were prepared using deionized (DI) water. All glassware cleaned with aqua regia, followed by copious washing with DI water before drying in an oven. Glassy carbon electrode (0.071cm^2 in area) was purchased from Tianjin Aida Tech. Co. Ltd., China.

Synthesis of Pt/ MoO_x-C

In a typical Pt/MoO_x-C preparation process, 20 mg of the obtained MoO_x-C was mixed with an approximate amount of Na_2PtCl_6 (2.56 mL, 10 mM) in an EG aqueous solution ($V_{\text{EG}}/V_{\text{water}} = 20 \text{ mL}/40 \text{ mL}$) under ultrasonication in a flask. The solution was then heated to 90 °C with a ramp rate of 10 °C min⁻¹ in an oil bath. The flask was capped with a condensing unit and maintained at 90 °C under mechanical stirring for 4 h. Finally, the mixture was filtered under vacuum to separate out the solid matter,

which was then rinsed several times with DI water and dried at 60 °C under vacuum for 12 h to obtain the Pt/MoO_x-C catalyst. For comparison, the catalyst of carbon-supported Pt NCs (Pt/C-H) was also prepared via the same procedure.

Characterizations

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed using JEOL 2100F microscope (JEOL; Japan) operated at 200 kV. The X-ray diffraction (XRD) spectra were conducted via a Rigaku D/Max-2500 X-ray diffractometer (Rigaku; Japan) with a Cu K_α source recorded. The X-ray photoelectron spectroscopy (XPS) data were collected using PHI-5000 versa probe (Ulvac-Phi; Japan) with an Al K_α source. Zeta potentials (ξ , effective surface charge) were measured by dynamic light scattering (Malvern Nano-ZS, UK). The inductively coupled plasma optical emission spectroscopy (ICP-OES) was tested by PerkinElmer Optima 8300 inductively coupled plasma emission spectrometer (PerkinElmer, USA). Raman spectra were recorded using a Renishaw 2000 system with an Argon ion laser (514.5 nm) and charge-coupled device detector.

Electrochemical measurements

The electrochemical measurements were conducted via a PARSTAT 2273 electrochemical workstation at room temperature. A three-electrode system which was composed of a glassy carbon electrode as the working electrode (0.071 cm² geometric area), a Pt sheet (2 × 2 cm²) as counter electrode and a saturated KCl Hg/HgCl₂ as reference electrode was employed for the electrochemical test. Typically, the as-prepared catalyst (2.0 mg) and Nafion solution (30 μL, 5.0 wt %) were dissolved in an ethanol aqueous (1 mL, $V_{ethanol}/V_{water} = 1/4$) and then sonicated for 30 min to form

a catalyst ink. Next, 3.0 μL of the catalyst ink was dropped onto the polished working electrode and dried in an oven at 60 $^{\circ}\text{C}$ for about 20 min. The metal mass was obtained from the total amount of catalyst on the electrode and the composition of the catalyst determined by ICP-OES. Subsequently, the working electrode covered with catalyst was activated in a N_2 -saturated 0.5 M H_2SO_4 solution via cyclic voltammetry (CV) between -0.2 V and 1.1 V at a scan rate of 50 mV s^{-1} until it approached to a steady state. The electrochemically active surface area (ECSA) of a catalyst can be calculated by measuring the charge collected in the hydrogen adsorption/desorption region after double-layer correction and assuming a value of 210 $\mu\text{C cm}^{-2}$ for the adsorption of a hydrogen monolayer in acid medium. The methanol electrooxidation was carried out in a N_2 -saturated aqueous solution containing 0.5 M H_2SO_4 and 1 M methanol also between -0.2 V and 1.1 V at a scan rate of 50 $\text{mV}\cdot\text{s}^{-1}$. Chronoamperometry (CA) tests were carried out at 0.6 V (vs. SCE) for a period of 9000 s.

Supporting figures

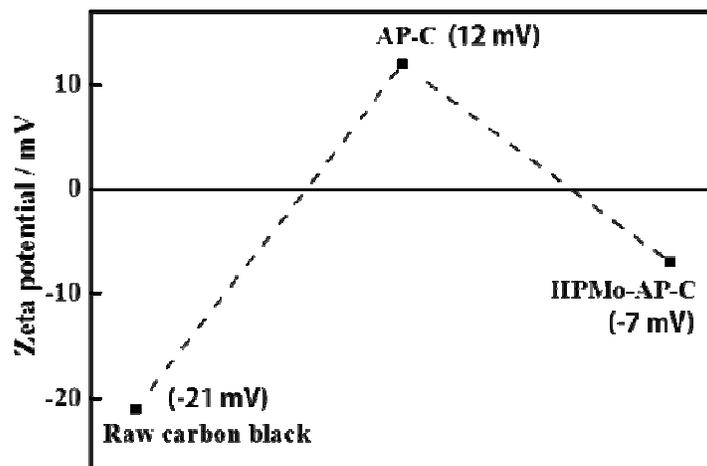


Fig. S1 Zeta potential of raw carbon black, AP-C and HPMo-AP-C.

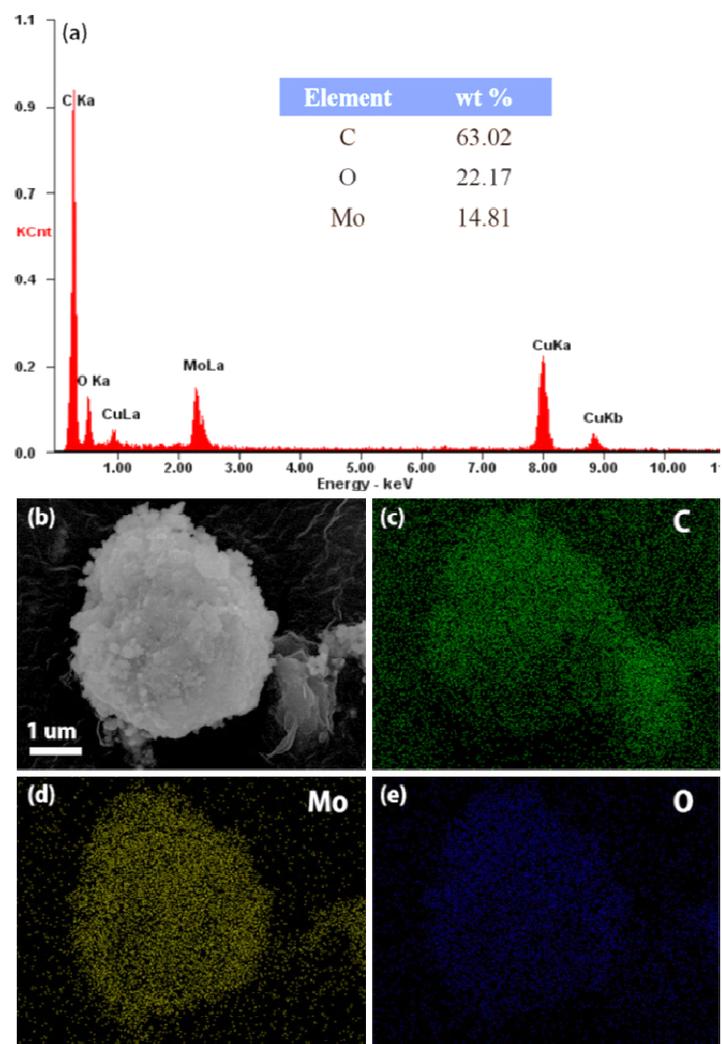


Fig. S2 (a) EDS and (b) SEM image of MoO_x-C, and element distributions of (c) C, (d) Mo and (e) O.

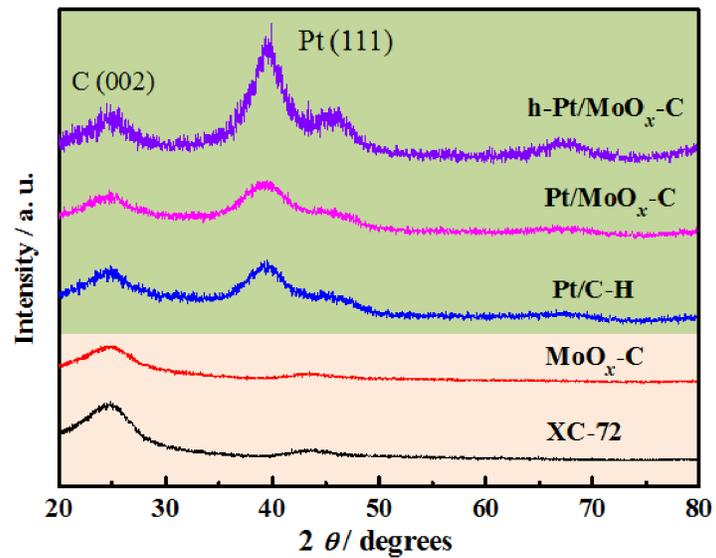


Fig. S3 XRD patterns of XC-72, MoO_x-C, Pt/C-H, Pt/MoO_x-C and h-Pt/MoO_x-C.

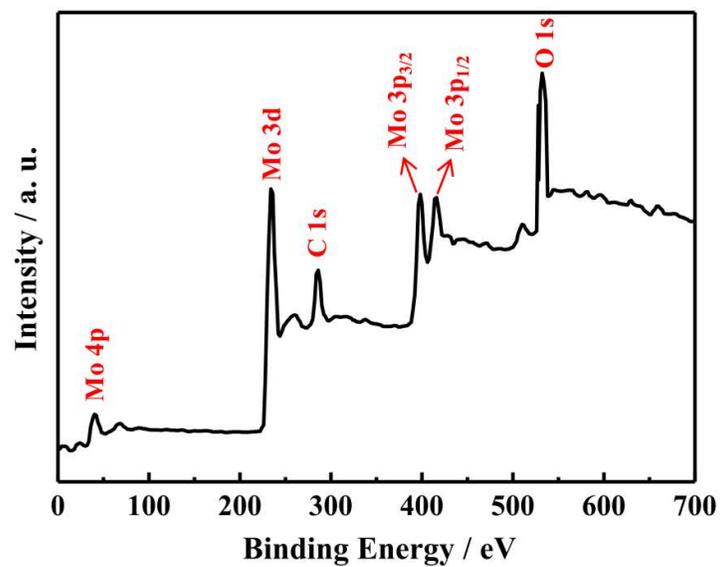


Fig. S4 XPS survey spectrum of MoO_x-C.

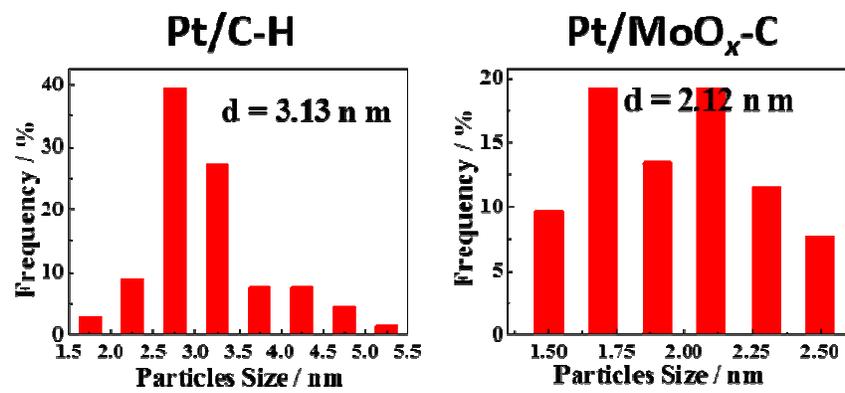


Fig. S5 Histograms of Pt particle diameters of Pt/C-H and Pt/MoO_x-C.

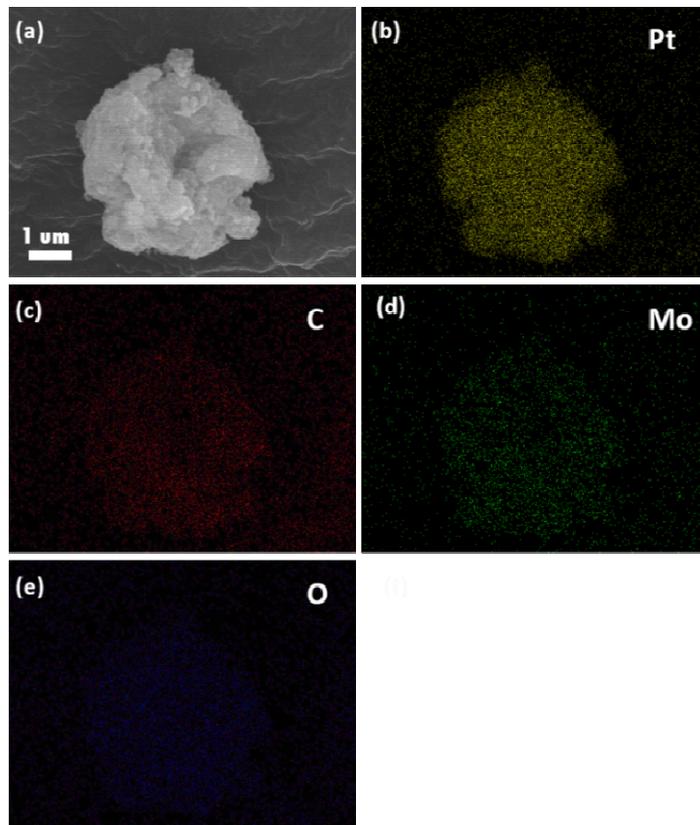


Fig. S6 (a) SEM image of h-Pt/MoO_x-C and element distributions of (b) Pt, (c) C, (d) Mo and (e) O.

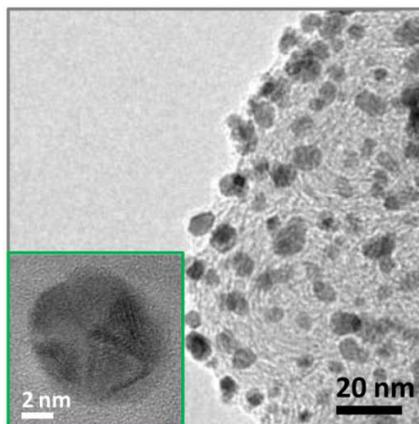


Fig. S7 TEM and HRTEM images of MoO_x-C supported Ag seeds.

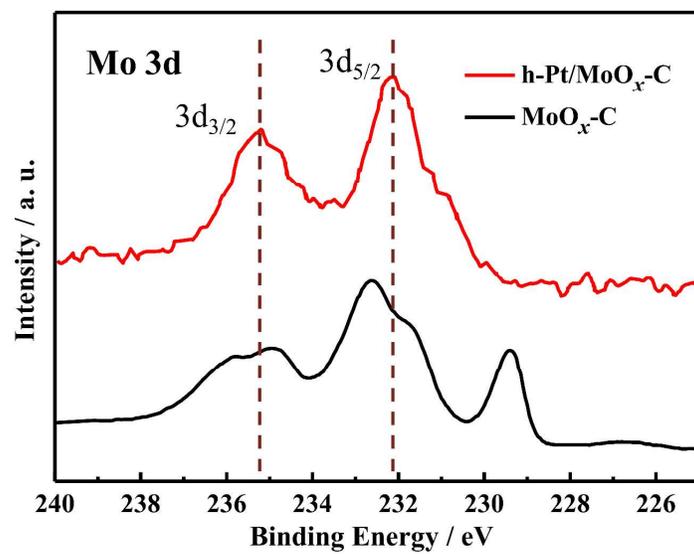


Fig. S8 XPS spectra Mo 3d for h-Pt/MoO_x-C catalyst and MoO_x-C support.

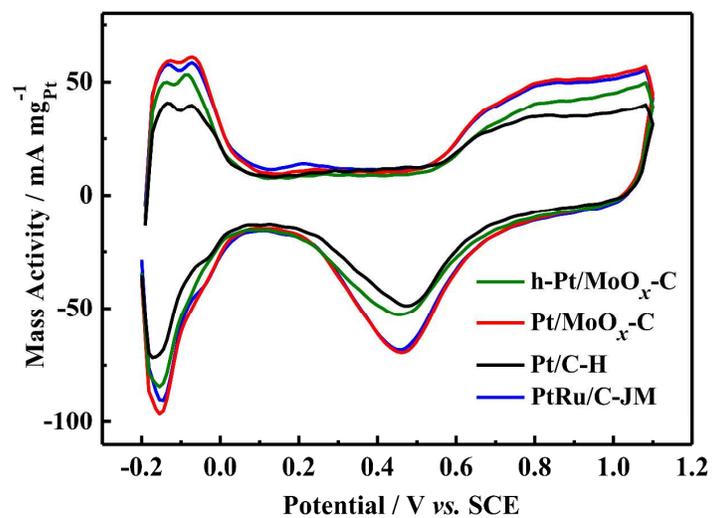


Fig. S9 Typical CVs of h-Pt/MoO_x-C, Pt/MoO_x-C, Pt/C-H and PtRu/C-JM catalysts in 0.5 M H₂SO₄.

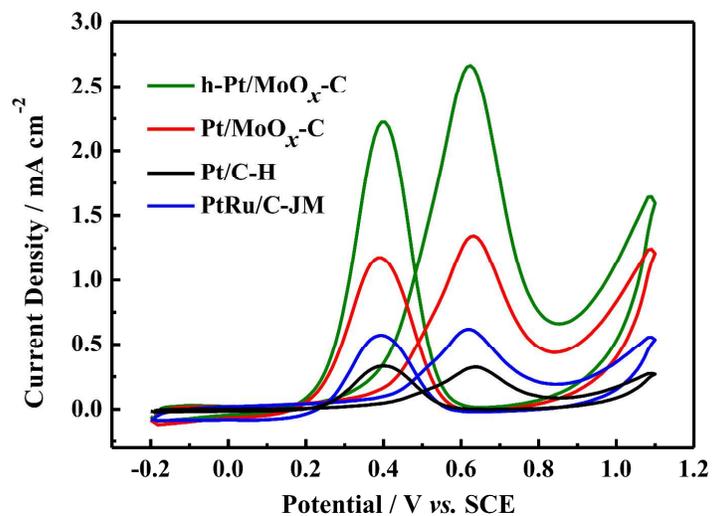


Fig. S10 Specific activity of h-Pt/MoO_x-C, Pt/MoO_x-C, Pt/C-H and PtRu/C-JM catalysts in 0.5 M H₂SO₄ solution containing 1.0 M CH₃OH, which are given as current densities normalized to the ECSA.

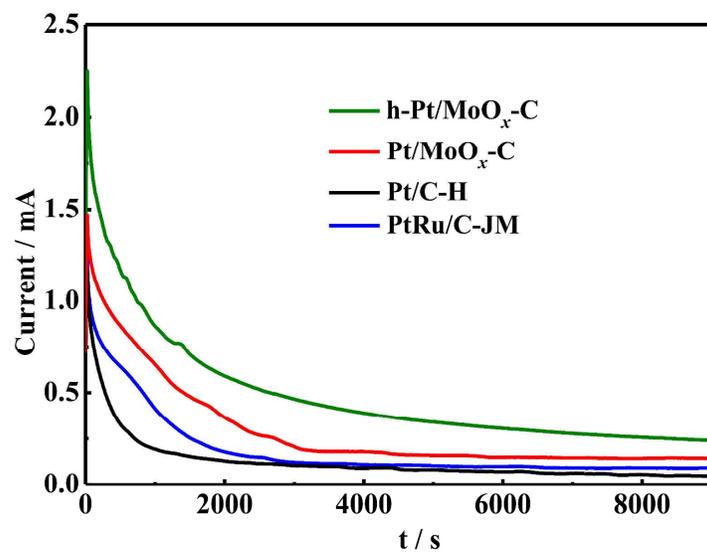


Fig. S11 CA curves of h-Pt/MoO_x-C, Pt/MoO_x-C, Pt/C-H and PtRu/C-JM catalysts in 0.5 M H₂SO₄ solution containing 1.0 M CH₃OH at 0.6 V for 9000 s.

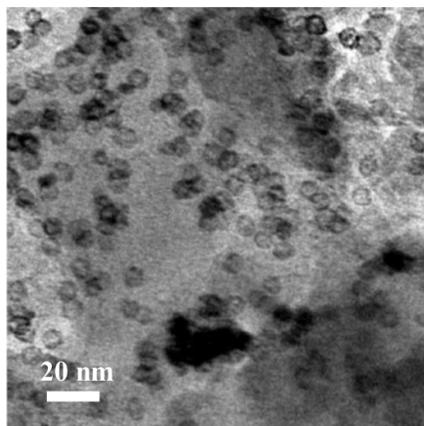


Fig. S12 Representative TEM image of the h-Pt/MoO_x-C catalyst after stability test.

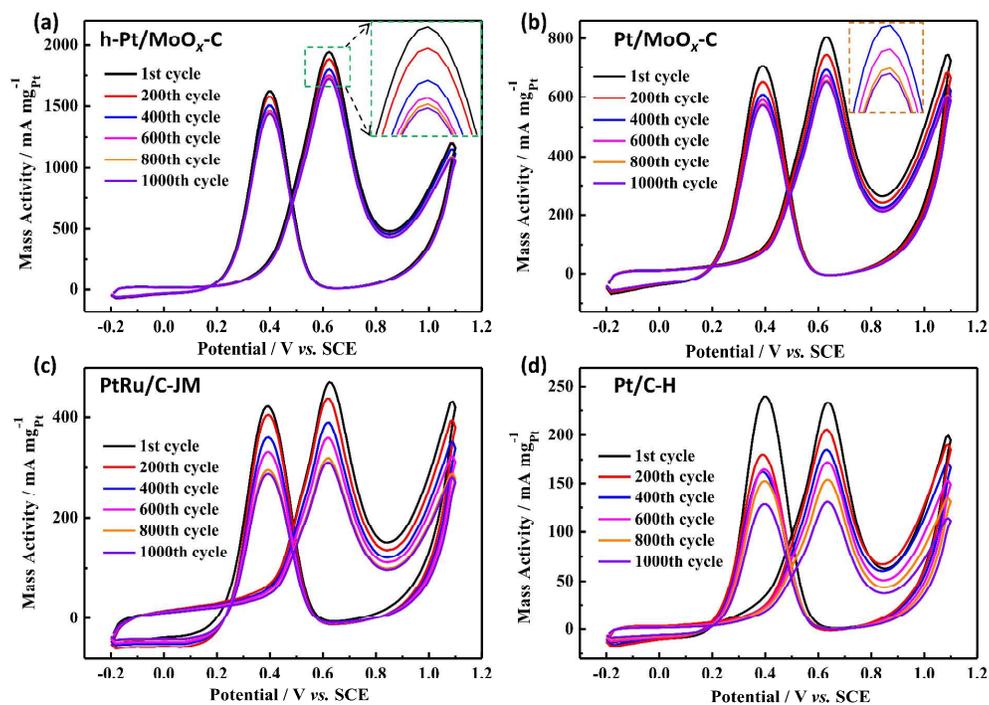


Fig. S13 The mass activities of h-Pt/MoO_x-C, Pt/MoO_x-C, PtRu/C-JM and Pt/C-H catalysts for the long cycle CV test in 0.5 M H₂SO₄ solution containing 1.0 M CH₃OH.

Supporting tables

Tab. S1 ECSAs, mass activities and i_j/i_b of h-Pt/MoO_x-C, Pt/MoO_x-C, PtRu/C-JM and Pt/C-H catalysts, respectively.

Sample	ECSA / m ² g ⁻¹	Mass activity / mA mg _{Pt} ⁻¹	i_j/i_b
h-Pt/MoO _x -C	56.4	1944.6	1.28
Pt/MoO _x -C	60.1	802.8	1.13
PtRu/C-JM	59.2	437.5	1.05
Pt/C-H	36.5	233.4	0.94

Tab. S2 The positive scan peak current density normalized as mass activity for the h-Pt/MoO_x-C catalyst and other recently reported catalysts.

Catalyst	Mass activity / mA mg _{Pt} ⁻¹	Scanning rate / mVs ⁻¹	Condition	References
h-Pt/MoO _x -C	1944.6	50	0.5 M H ₂ SO ₄ + 1.0 M CH ₃ OH	This work
Pt-Ni ₂ P/C-30%	1432	50	0.5 M H ₂ SO ₄ + 1.0 M CH ₃ OH	1
Pt/MnO _x -MWCNTs	1367.3	50	0.5 M H ₂ SO ₄ + 1.0 M CH ₃ OH	2
Pt/MnO ₂ /GS	1224	20	1.0 M H ₂ SO ₄ + 2.0 M CH ₃ OH	3
Pt-SiO ₂ /graphene	1047	50	0.5 M H ₂ SO ₄ + 1.0 M CH ₃ OH	4
Pt/Ce _{0.8} Sn _{0.2} O _{2-δ} -C	502	50	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH	5
Pt/Ti _{0.9} Sn _{0.1} O ₂ -C	459.6	10	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH	6
Pt/CeO ₂ /graphene	366	100	0.5 M H ₂ SO ₄ + 1.0 M CH ₃ OH	7
Pt/CeO ₂ /PANI	361.33	100	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH	8
Pt/TiO ₂ @N-doped C-900	490	50	0.5 M H ₂ SO ₄ + 1.0 M CH ₃ OH	9
Pt-MoO _x /CNTs	246.2	20	0.5 M H ₂ SO ₄ + 1.0 M CH ₃ OH	10
Pt/TiO ₂ -C	102.8	50	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH	11

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