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Supporting Information

for

Carbon-supported Pt_5P_2 nanoparticles used as a high-

performance electrocatalyst for methanol oxidation reaction

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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 section

Materials

Chloroplatinic acid (H₂PtCl₆) was purchased from Sigma-Aldrich Chem. Co., USA). sodium hypophosphite (NaH₂PO₂·H₂O), dibasic sodium phosphate (Na₂HPO₄), ethylene glycol (EG), methanol, sulfuric acid (H₂SO₄), and other chemical reagents were purchased from Sinopharm Chemical Reagent 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. All aqueous solutions were prepared using deionized (DI) water. High purity nitrogen (\geq 99.99%) was supplied by Nanjing Special Gas Factory Co., Ltd., China. Glassy carbon electrode (0.071cm² in area) was purchased from Tianjin Aida Tech. Co. Ltd., China.

Synthesis of Pt/C

In the standard synthetic strategy, 60 mg carbon black (Vulcan XC-72) were firstly well-dispersed in a mixed solution containing 20 mL of H₂O and 20 mL of EG by ultrasonication. Then, 7.68 mL of 10 mM H₂PtCl₆ aqueous solution was added into the above black suspension and magnetically stirred for 0.5 h. Immediately, the resulting mixture was heated to 125 °C under reflux at a ramping rate of 10 °C /min and maintained at that temperature for 4 h while stirring at a rate of 600 rpm. Finally, the resulting mixture was subjected to filter under vacuum to separate out the solid matter, which was then rinsed with deionized water several times and dried at 60 °C under vacuum for 12 h to obtain the Pt/C catalyst.

Characterizations

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed using JEOL 2100F microscope (JEOL; Japan) operated at 200 kV. Energy dispersive X-ray spectroscopy (EDS) analysis and high-angle annular dark-field scanning TEM (HAADF-STEM) were also conducted using the same instrument to identify the elemental composition of the products. All the samples for TEM study were prepared by dropping an ethanol diluted suspension of the catalyst onto a copper grid coated with carbon film. The powder X-ray diffraction (PXRD) patterns were conducted via a Rigaku D/Max-2500 X-ray diffractometer (Rigaku; Japan) with a Cu K_{α} source recorded. Deconvolution of the multicomponent PXRD pattern was carried out using PeakFit software (Aisn Software Inc). The X-ray photoelectron spectroscopy (XPS) data were collected using PHI-5000 versa probe (Ulvac-Phi; Japan) with an Al K_{α} source. All the spectra were corrected using C 1s signal located at 284.5 eV. Deconvolution of the spectra was carried out using the software XPS Peak 4.1 with thoroughly considering the constraints on binding energy, peak area and full width at half maximum. Metal contents in all catalysts were determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES, TJA RADIAL IRIS 1000 ICP-AES).

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 (0.071cm² 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 °C for about 20 min, and the catalyst weight on the working electrode is 0.2 mg. Subsequently, the working electrode covered with catalyst was activated in a N₂-saturated 0.5 M H₂SO₄ solution via cyclic voltammetry (CV) between -0.2 V and 1.1 V at a scan rate of 20 mV s⁻¹ until it approached to a steady state. The electrochemically active surface area (ECSA) of a catalyst can calculated by measuring the charge collected in the hydrogen adsorption/desorption region after double-layer correction and assuming a value of 210 uC cm⁻² for the adsorption of a hydrogen monolayer under acid medium. 99.99% pure CO was purged to the cells filled with 0.5 M H₂SO₄ electrolyte for 30 min while the working electrode was held at 0.2 V (vs. SCE). N2 was then purged to the system for 30 min to remove non-adsorbed CO before the measurements were made. The CO stripping was performed in the potential range of $-0.2 \sim 1.1$ V at a scan rate of 50 mV s⁻². The ECSA and the CO tolerance were estimated by the CO stripping test, assuming that the Coulombic charge required for the oxidation of the CO monolayer was 420 μ C cm⁻². The methanol electrooxidation was carried out in a N2-saturated aqueous solution containing 0.5 M H2SO4 and 1.0 M methanol also between $-0.2 \sim 1.1$ V at a scan rate of 20 mV·s⁻¹. Chronoamperometry (CA) tests were carried out at 0.6 V (vs. SCE) for a period of 3600 s. The long-term durability of the catalysts was carried out in a N₂-saturated aqueous solution containing 0.5 M H₂SO₄ and 1.0 M methanol by a continuous 2000 and 5000 potential cycles

between -0.2 V and 1.1 V at a scan rate of 20 mV·s⁻¹. To estimate the stability of the catalysts, the chronoamperometric (CA) experiments were performed in still 0.5 M H₂SO₄ and 1 M CH₃OH solutions at 0.6 V. The electrochemical impedance spectroscopy (EIS) was recorded at 0.6 V (*vs.* SCE) over a frequency range from 100 kHz to 10 mHz with 10 points per decade. The amplitude of the sinusoidal potential signal was 10 mV, and the ZSimpWin software was used to analyze the impedance data.

Supporting Figures



Figure S1 (a) TEM and (b) HRTEM images of carbon black support used in this work.



Figure S2 PXRD patterns of (a) XC-72; (b) the sample that obtained by the standard synthetic strategy in absence of H_2PtCl_6 ; (c) Pt/C synthesized by the standard synthetic strategy in absence of NaH_2PO_2 and Na_2HPO_4 .



Figure S3 XPS spectra of (a) XC-72; (b) the sample that obtained by the standard synthetic strategy in absence of H_2PtCl_6 ; (c) Pt_5P_2/C .



Figure S4 (a) TEM and HRTEM images and (b) the particle-size histogram of Pt/C synthesized by the standard synthetic strategy in absence of NaH₂PO₂ and Na₂HPO₄.



Figure S5 The TEM images of the products that synthesized by the standard synthetic strategy as that of Pt_5P_2/C but in the absence of (a) Na_2HPO_4 , (b) NaH_2PO_2 , and (c) the corresponding PXRD patterns.



Figure S6 The TEM images of the products that synthesized by the standard synthetic strategy as that of Pt_5P_2/C except the use different molar ratios of Na_2HPO_4/NaH_2PO_2 : (a) 0.025/0.05, (b) 0.1/0.05; and (c) the corresponding PXRD patterns.



Figure S7 TEM image of the commercial PtRu/C-JM (20 wt% Pt + 10 wt% Ru).



Figure S8 Typical CVs of Pt_5P_2/C , Pt/C and PtRu/C-JM catalysts for MOR in N_2 -saturated 0.5 M H₂SO₄ solution containing 1.0 M CH₃OH with a scan rate of 20 mV s⁻¹.



Figure S9 Linear sweep voltammetry of Pt_5P_2/C , Pt/C and PtRu/C-JM catalysts in N₂-saturated 0.5 M H₂SO₄ solution containing 1.0 M CH₃OH with a scan rate of 20 mV s⁻¹.



Figure S10 (a) Nyquist plots of Pt_5P_2/C , Pt/C and PtRu/C-JM catalysts located in the first quadrant for methanol oxidation at 0.6 V (*vs.* SCE); (b) Equivalent circuits used for methanol oxidations in this work, Q_{dl} is a CPE representing the double layer.



Figure S11 (a) The particle-size histogram and (b) HRTEM images of Pt_5P_2/C after 5000 CV cycles.



Figure S12 PXRD pattern of Pt_5P_2/C after ADTs of 5000 cycles.

Supporting Tables

Table S1 The Pt loadings, P loadings and Ru loadings of Pt_5P_2/C , Pt/C and PtRu/C-JM

Catalant	Pt ₅ P ₂ /C		Pt/C		PtRu/C-JM	
Catalyst	before	after	before	after	before	after
Pt / wt %	16.7	15.4	17.6	12.1	18.1	15.3
P / wt %	1.06	0.98	-	-	-	-
Ru / wt %	-	-	-	-	9.2	7.5

catalysts measured by ICP-AES before and after ADT of 5000 cycles.

2 <i>θ</i> / °	(h k l)	<i>d</i> / nm
34.13	(311)	0.262
38.52	(-402)	0.234
38.59	(-221)	0.233
40.11	(-113)	0.225
41.58	(022)	0.217
48.10	(420)	0.189

Table S2 Parameters of the broadened diffraction peak located at about 40° from thePXRD pattern of Pt_5P_2/C and its related profile-fitting results.

 Catalyst
 ECSA^a / m² g_{Pt}⁻¹
 ECSA^b / m² g_{Pt}⁻¹
 Peak potential / V vs. SCE

 Pt₅P₂/C
 56.8
 58.2
 0.427

 Pt/C
 47.2
 46.9
 0.564

 PtRu/C-JM
 49.6
 49.1
 0.602

Table S3 Electrochemical surface area (ECSA) estimated from hydrogen absorption

 and CO stripping experiments and the peak potentials for CO stripping.

^a The ECSA of the catalysts integration from the hydrogen absorption.

^b The ECSA of the catalysts integration from the CO stripping experiment.

Table S4 The specific activity (SA) and mass activity (MA) of Pt_5P_2/C , Pt/C and PtRu/C-JM catalysts.

Catalyst	SA ^a / A m ⁻²	SA^b / A m⁻²	MA / A mg _{Pt} ⁻¹
Pt ₅ P ₂ /C	63.43	61.90	3.603
Pt/C	6.95	6.99	0.328
PtRu/C-JM	7.98	8.06	0.396

^a The SA of the catalysts integration from the hydrogen absorption.

^b The SA of the catalysts integration from the CO stripping experiment.

Table S5 Impedance parameters obtained by fitting the experimental data in Figure 3e.

Sample	$R_{\rm s}$ / Ω	$Q_{ m dl}$ × 10 ⁻³ / s ⁿ Ω^{-1}	$R_{ m ct}$ / Ω	C_1 / mF	R_1 / k Ω
Pt_5P_2/C	0.65	157.5	-332.7	-246.2	-0.06
PtRu/C-JM	1.08	73.1	-692.6	-175.3	-1.12
Pt/C	1.23	61.8	-778.5	-151.6	-1.29

Catalyst	Test condition	MA / A mg _{Pt} ⁻¹	SA / A m ⁻²	Ref.
Pt ₅ P ₂ /C	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH	3.603	63.43	This work
Pt NWs	0.1 M HClO ₄ + 0.1 M CH ₃ OH	1.312	58.4	1
Pt/I-IL (10)/GNPs	0.5 M H ₂ SO ₄ + 1.0 M CH ₃ OH	1.560	25.7	2
Pt/R-3DNG	$1.0 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{OH}$	1.63	35.6	3
Pt-Ni ₂ P/C	0.5 M H ₂ SO ₄ + 1.0 M CH ₃ OH	1.431	40.4	4
PtCu nanoring	0.5 M H ₂ SO ₄ + 1.0 M CH ₃ OH	2.175	52.6	5
Pt ₁ Cu ₁ -AA NTs	0.5 M H ₂ SO ₄ + 1.0 M CH ₃ OH	2.252	60.9	6
Pt-Ni-P MNCs	0.5 M H ₂ SO ₄ + 1.0 M CH ₃ OH	1.21	23.5	7
Pt-Ni-Cu ERDs	0.5 M H ₂ SO ₄ + 1.0 M CH ₃ OH	2.39	38.8	8
PtRu NWs	0.1 M HClO ₄ + 0.5 M CH ₃ OH	0.82	11.6	9
PtBi nanoplates/C	0.1 M HClO ₄ + 0.1 M CH ₃ OH	1.1	31.8	10
Pt ₉₅ Co ₅ NWs	0.5 M H ₂ SO ₄ + 1.0 M CH ₃ OH	0.491	21.3	11
Pt _{3.5} Pb NNWs	0.5 M H ₂ SO ₄ + 1.0 M CH ₃ OH	1.18	27.8	12
Pt-BTO4/BC	0.5 M H ₂ SO ₄ + 1.0 M CH ₃ OH	2.72	48.7	13
h-Pt/MoO _x -C	0.5 M H ₂ SO ₄ + 1.0 M CH ₃ OH	1.944	34.5	14
Pt/Ce _{0.7} Mo _{0.3} O _{2-δ} -C	0.5 M H ₂ SO ₄ + 1.0 M CH ₃ OH	1.888	20.1	15

 Table S6 List of up-to-date MOR nanocatalysts reported.

Catalyst	Initial / A mg _{Pt} -1	2000 cycles / A mg _{Pt} ⁻¹	5000 cycles / A mg _{Pt} ⁻¹
Pt ₅ P ₂ /C	3.603 (100%)	3.462 (96.1%)	3.178 (88.2%)
PtRu/C-JM	0.328 (100%)	0.294 (89.6%)	0.245 (74.8%)
Pt/C	0.396 (100%)	0.338 (85.3%)	0.276 (69.7%)

Table S7 The retentions in MA for Pt_5P_2/C , Pt/C and PtRu/C-JM after 2000 and 10000

CV cycles.

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