Supporting information

Pt/C electrocatalyst derived from recycled Pt/Re mixed solution: synthesis, characterization, and electrochemical behavior in fuel cell

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1. Materials

The spent catalyst was obtained by China National Petroleum Corporation (CNPC). Carbon black Vulcan XC-72R was purchased from Cabot, China. Chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, 99.9%, Pt:37.5%+) was obtained from Adamas, China. Ethylene glycol (EG, 99%) were purchased from Innochem, China. Sodium hydroxide (NaOH, 96%), Sodium carbonate (Na_2CO_3) and perchloric acid ($HClO_4$, 70%) were purchased from Aladdin, China. Isopropyl alcohol (IPA, ≥99.7%) , Hydrochloric acid (HCl, 36-38%), Hydrogen peroxide (H_2O_2, ⩾30%) and Sulfuric acid (H_2SO_4, 95-98%)were purchased from Greagent, China. The D520 Nafion solution (5 wt%) and D2020 Nafion solution (20 wt%) was obtained from Dupont. The 20 wt% commercial Pt/C and 60 wt% commercial Pt/C were obtained from (TANAKA, Japan.) and Wuhan Himalaya Technology Co., China. Deionized water was obtained through an ultra-pure purification system. All reagents were of analytical grade and were used with no further purification.

2. Characterization

UV-vis spectrophotometry (UV-2600, Japan) was applied to trace the coordination process. X-ray diffraction (XRD) measurements were performed, using a diffractometer (DX2700BH, China) with Cu Kα radiation. ICP-OES inductively coupled plasma optical emission spectroscopy (Avio 200) was used to determine the loadings of Pt in the catalysts; the mass activity was further obtained according to Pt loading. The surface morphologies of the MW-Pt/C and TANAKA 20 wt% commercial Pt/C catalysts were observed by field emission transmission electron microscope

(Tecnai G2 F20 S-Twin, American). The X-ray photoelectron spectroscopy spectra (XPS) were collected by XPS (Thermo Fisher ESCALAB 250Xi).

Calculation of Pt nanoparticle size based on XRD can be calculated by the Scherrer formula[1, 2]:

$$\bar{D}=K\lambda/(FWHM\cos\theta)$$

where λ is the wavelength, $\bar{D}$ is the volume averaged particle size, K = 0.89 is the Scherrer constant, FWHM is the full width at half-maximum of the peak, and θ, the Bragg angle of the [hkl] reflection.

3. Electrode preparation

2.5 mg of catalyst was ultrasonically dispersed in 1 mL of solution containing 800 μL of IPA, 180 μL of water and 20 μL of Nafion solution for 30 min. The glassy carbon electrode surface was wiped by a polishing kit with 0.05 μm alumina particles which were later washed with deionized water. After a uniform mixture formed 10 μL of the above solution was coated to a precleaned glassy carbon electrode (area=0.19625 cm^2). The Pt loading is about 25.48 $\mu g_{Pt}/cm^2$. TANAKA 20 wt% commercial Pt/C ink was also prepared and coated as per similar Pt loading achieved.

4. Electrochemical tests

Electrochemical measurements were performed on a CHI 760 electrochemical workstation combined with a RDE (ALS, Japan). The working electrode is a glassy carbon electrode with a diameter of 5 mm. The counter electrode is a carbon electrode, and the reference electrode is a Hg/Hg_2SO_4 electrode, the potentials measured using the Hg/Hg_2SO_4 electrode can be converted to RHE by the following equation[3, 4]:

$$E\ (vs.\ RHE) = E\ (vs.\ Hg/Hg_2SO_4) + 0.652 + 0.0592pH$$

Cyclic voltammogram (CV) were measured in reference to the RHE in N_2 saturated 0.1 mol/L $HClO_4$ from 0.05 V to 1.1 V at a scan rate of 50 mV/s. Linear sweep voltammetry (LSV) curves were measured in reference to RHE in O_2-saturated 0.1 M $HClO_4$ electrolyte from 0.05 V to 1.1 V at a scan rate of 10 mV/s and a rotating speed of 1600 rpm. To further evaluate the electrochemical durability of the Pt-NPC, an accelerated degradation test (ADT) was carried out in reference to RHE in O_2 saturated 0.1 mol/L $HClO_4$ at scan rate of 100 mV/s for 5000 cycles at 0.6–1.1 V. The electrochemically active surface area (ECSA) was calculated based on the hydrogen underpotential deposition (HUPD) method with the following equation[5, 6]:

$$ECSA = \frac{Q_H}{2.1 \times M_{Pt} \times \nu} (m^2 / g_{Pt}) \quad (1)$$

where Q_H is the charge from the hydrogen adsorption/desorption (HAD) region of CVs; M_{Pt} represents Pt loading on the glassy carbon electrode (g); υ represents the scan rate (V/s).

The mass activity (MA) and specific activity (SA) were calculated by the following formula[5, 7]:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_L} \quad (2)$$

$$MA = \frac{j_k \times S}{M_{Pt}} (A / mg_{Pt}) \quad (3)$$

$$SA = \frac{100 \times j_k \times S}{M_{Pt} \times ECSA} (mA / cm^2) \quad (4)$$

where j represents the current density measured by the experiment (mA/cm^2); j_k represents the dynamic current density (mA/cm^2); j_L is the limiting current diffusion

density measured by the experiment (mA/cm^2). S is the electrode area (cm^2). M_{Pt} is the loading of Pt (g).

5. MEA measurement

Membrane electrode assemblies (MEAs) were prepared with M-50 (20 wt%) and TANAKA 20 wt% commercial Pt/C as the cathode, respectively. Commercial Pt/C (60 wt%, Wuhan Himalaya Optoelectronics Technology Co., Ltd.) was used as the anode. The Nafion ionomer (D2020, Dupont). 37 mg catalysts, 6.4 g water, 60 mg ionomer and 6.5 g IPA are mixed uniformly under ultrasonic treatment to obtain catalyst slurry. The prepared catalyst inks were directly coated on a M820.15 membrane (Gore, 15 μm). The cathode catalyst loadings were both 0.1 mg_{Pt}/cm^2 for M-50 and TANAKA 20 wt% commercial Pt/C, with corresponding anode catalyst loading of 0.1mg_{Pt}/cm^2. The prepared MEAs (5 cm^2 active electrode area) were hot-pressed with the gas diffusion layer (GDL, Sigracet 29BC, 0.235±0.025 nm) at 130 °C and pressure of 1.4 MPa for 2 minutes. Performance of the single cells was all measured at 85 ℃ with a back-pressure of 0.15 MPa using a fuel cell test station (HS330). To measure I-V polarization curves, 80 ℃ and 100% humidified hydrogen (800 sccm) and oxygen (1500 sccm) were supplied into the anode and cathode, respectively.

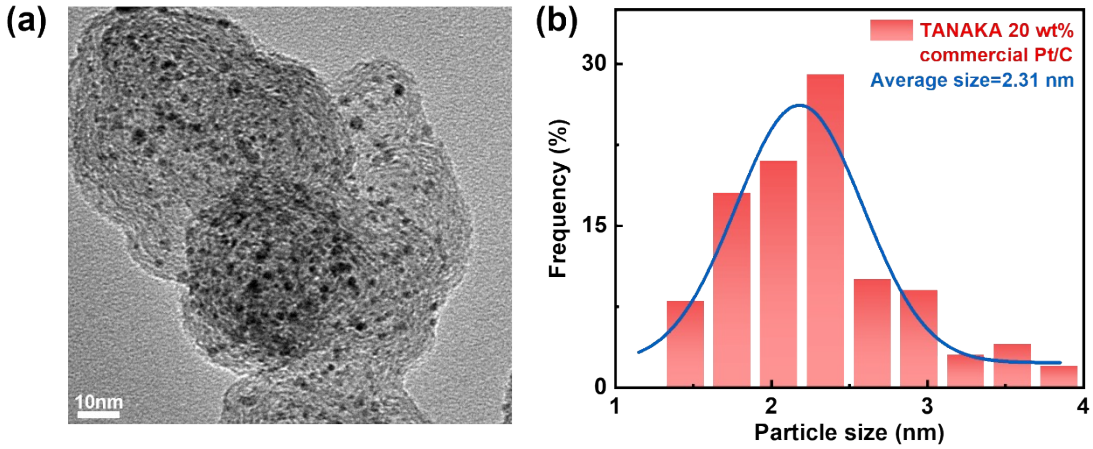

Fig. S1 (a) TEM image of TANAKA 20 wt% commercial Pt/C; (b) Pt nanoparticles size distribution.

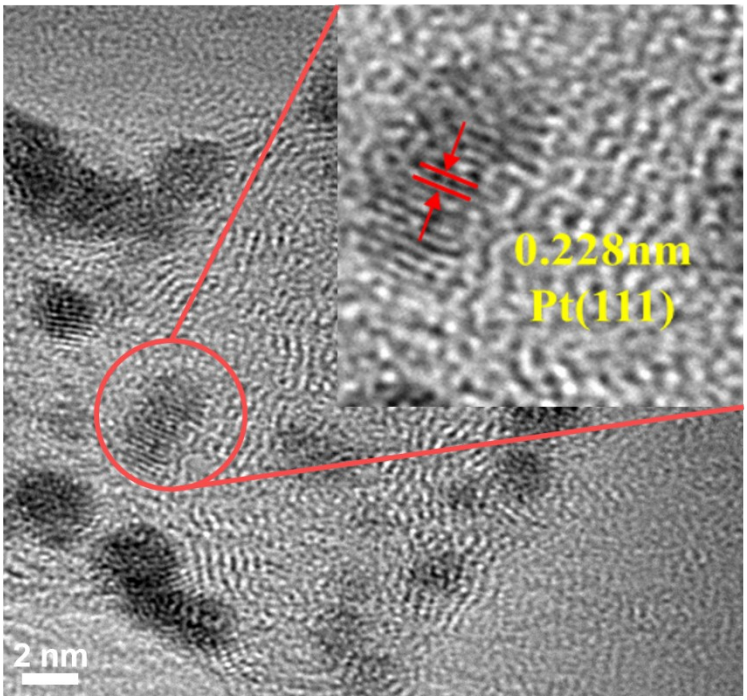

Fig. S2 High-resolution TEM image of M-50.

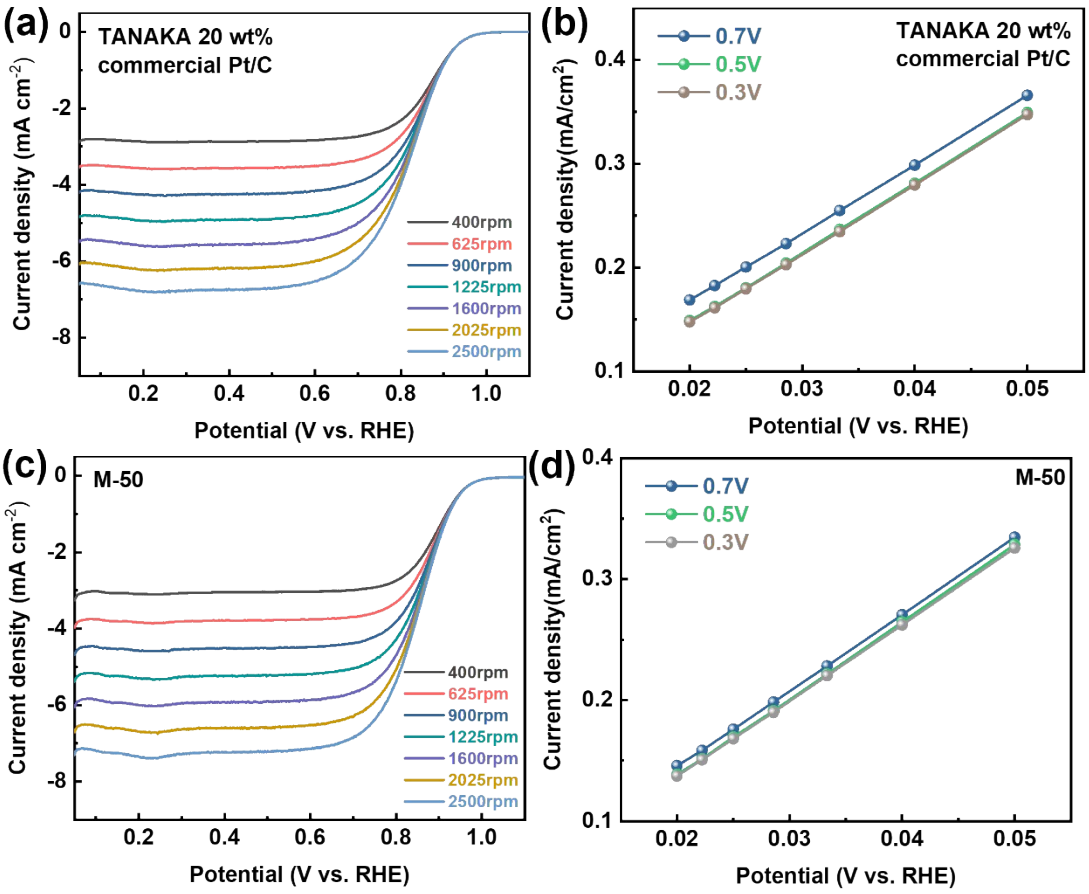

Fig. S3 LSV curves at various rotation rates and the Koutecky-Levich plots that was obtained at 0.3 V, 0.5 V and 0.7 V versus RHE of TANAKA 20 wt% commercial Pt/C (a,b) and M-50 (c,d).

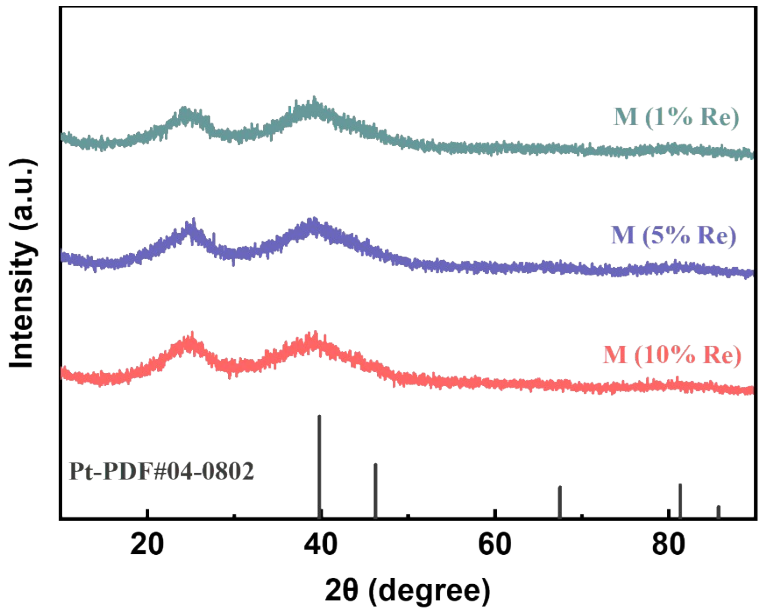

Fig.S4 The X-ray diffraction patterns of M (Re) electrocatalysts.

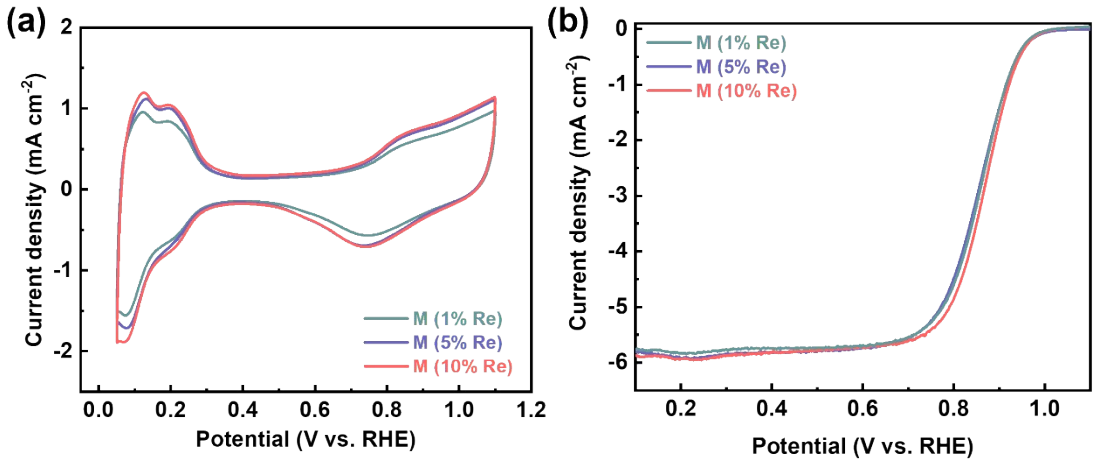

Fig.S5 The electrochemical tests of M (Re) electrocatalysts (a) CV; (b) LSV.

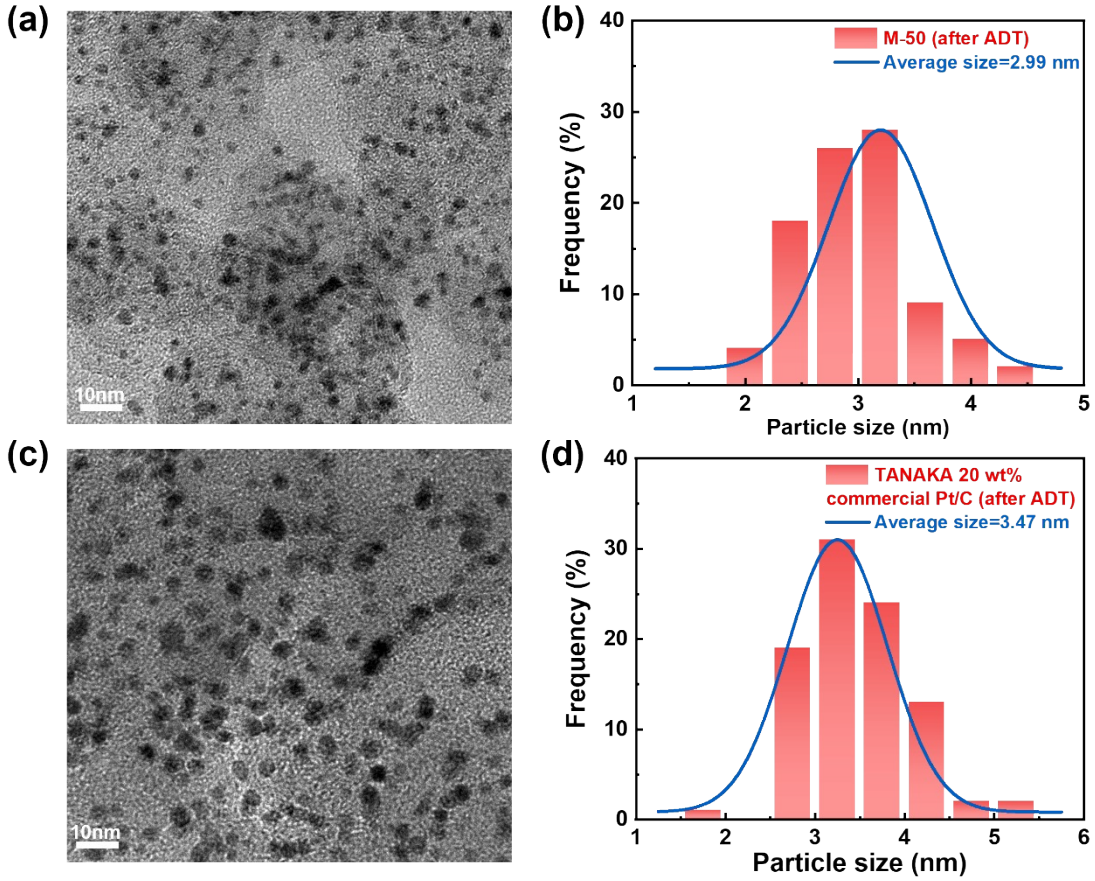

Fig. S6 TEM image of electrocatalysts and Pt size distribution: (a, b) M-50; (c, d) TANAKA 20 wt% commercial Pt/C.

Table S1. The contents of Pt and Re in the M(Re) electrocatalysts were determined by ICP-OES.

Samples	Pt (wt%)	Re (wt%)
M(1%Re)	19.75	—
M(5%Re)	19.54	—
M(10%Re)	19.28	—

Table S2. The contents of Pt in the electrocatalysts were determined by ICP-OES.

Samples	Pt (wt%)
M-110	20.67
M-80	21.18
M-50	19.41
M-20	19.93
TANAKA 20 wt% commercial Pt/C	19.98

Table S3. The FWHM (full width at half maxima) and Pt particle size according to XRD and TEM information of electrocatalysts.

Samples	FWHM	Crystallite size according to XRD pattern (nm)	Particle size according to TEM image (nm)
M-110	1.70265	5.18	2.94
M-80	5.13973	1.71	2.21
M-50	6.27061	1.41	2.04
M-20	8.03012	1.10	1.83
TANAKA 20 wt% commercial Pt/C	3.22893	2.73	2.31

Table S4. Electrochemical performance of electrocatalysts.

Catalysts	$E_{1/2}$ (V vs.RHE)	ECSA (m^2/g_{Pt})	MA (A/mg_{Pt})	SA (mA/cm^2)
M-110	0.8372	41.38	0.0428	0.1035
M-80	0.8522	58.61	0.0653	0.1114
M-50	0.8622	109.81	0.0890	0.0810
M-20	0.8542	62.04	0.0657	0.1060
TANAKA 20 wt% commercial Pt/C	0.8472	44.01	0.0592	0.1345

References

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