

Supporting Information

“One Stone Three Birds” of A Synergetic Effect between Pt Single Atoms and Clusters Makes an Ideal Anode Catalyst for Fuel Cells

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1. Experimental sections

1.1 Chemicals

Vulcan XC-72 was purchased from Cabot and ascorbic acid ($C_6H_8O_6$, 99%) was obtained from Aladdin. Ultrapure water was used in all experiments. Commercial Pt/C (20 wt%) was purchased from Johnson-Matthey. All the chemicals were used as delivered without further treatment.

1.2 Catalyst synthesis

For the synthesis of Pt_x -C-AA, based on literature¹, we firstly treated 500 mg Vulcan XC-72 with 176 mg ascorbic acid (AA) in 175 mL ultrapure water at room temperature for 3 h by stirring so that ascorbic acid could fully etch the carbon carrier, after further washing by centrifugation and drying, a dry powder named as C-AA was obtained, next, 140 mg C-AA powder was ultrasonically dispersed in ultrapure water with different amount of H_2PtCl_6 to achieve different Pt dosage varied from 1.0, 1.5, 2.0, 2.2, 3.0 to 3.5 wt%, respectively. After stirring for 3 h at room temperature, the obtained Pt-C-AA precursors with different Pt loadings were washed by centrifugation and dried. The obtained powders were then calcined in air at 300 °C for 1 h to obtain the final catalyst samples. It was found that the optimal Pt dosage was 2.5 wt%, corresponding to a final Pt loading of 1.7 wt% on optimal Pt-C-AA.

1.3 Physical characterizations

The morphology of as-prepared samples were obtained using transmission electron microscopy (TEM) on a JEM-2100F microscopy with an accelerating voltage of 200 kV, and configured high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) to perform element mapping analysis on the selected area. The dispersion of Pt was characterized by spherical aberration corrected scanning transmission electron microscopy (Cs-STEM) on a JEOL JEM-ARM200F instrument. X-ray diffraction (XRD) spectrum was obtained from Bruker *D8 ADVANCE* X-ray Diffractometer using Cu $K\alpha$ radiation ($\lambda=0.15418$ nm). The Raman spectrum was obtained by T64000 laser confocal Raman spectroscopy employing the Nd: YAG laser wavelength of 532 nm. Obtained by N_2 desorption and adsorption curve on the ASAP 2020 instrument at a temperature of 77 K. X-ray photoelectron spectroscopy (XPS) measurements were performed on an AXIS Ultra DLD using a monochromic Al X-ray source. The loading of Pt was determined by an inductively coupled spectrometry (ICP-MS) (ICAP-6000, Thermo Fisher Scientific).

1.4 Electrochemical characterizations

The electrocatalytic activity evaluation adopted the rotating disk electrode (RDE) method. A catalyst ink was prepared by ultrasonically dispersing 5 mg of the catalyst powders in a mixed solution of 950 μ L of ethanol and 50 μ L of 5 wt% Nafion solution. Use a micropipette to pipette 10 μ L of the prepared catalyst ink droplet on a 0.1256 cm^2 of glassy carbon electrode as the working electrode, which was about 0.39 $mg\ cm^{-2}$ of the total catalyst load. We chose a carbon rod as the counter electrode, and an Ag/AgCl electrode filled with saturated potassium chloride as the reference electrode. Then all potentials were

converted to a reversible hydrogen electrode (RHE) reference scale. As a reference, Pt-C and Pt/C_{com} (Johnson Matthey) working electrodes were obtained by the same method, and the catalysts loading were both 0.39 mg cm⁻². All measurements were performed in an aqueous solution of 0.1 M HClO₄ at 25 °C. At a potential between 0 ~ 1.2 V and in a scan rate of 50 mV s⁻¹, cyclic voltammetry (CV) was measured without rotation by using nitrogen and hydrogen as a saturated gas, respectively. The HOR activity was measured by linear sweep voltammetry (LSV) in the potential range of 0 ~ 0.4 V at 200、400、900、1600 and 2500 rpm, respectively, which the aqueous solution had been saturated with hydrogen for 30 minutes before the measurement. ORR activity was obtained by measuring the LSV curve at 1600 rpm with saturated oxygen. When measuring the CO-tolerance test, it was ensure that the surface of each electrode was loaded with the same mass of Pt (6.73 μg cm⁻²).

1.5 MEA preparation and PEMFC test

The catalyst ink for MEA assembly was prepared by ultrasonic dispersing the mixture of catalysts, 5 wt% Nafion solution and water/isopropanol (1:1) solvent for more than 1 hour. The concentration of catalysts in the final ink was controlled at 12 mg_{catalyst} mL⁻¹, and the concentration of Nafion was controlled at 5.2 mg mL⁻¹ to ensure that the total mass in the catalytic layer was 30 wt%. Then, the ink was sprayed on both sides of Gore film (20 μm, W. L. Gore & Associates) by using a spray gun with model USTAR S130. The effective area of MEA is 4 cm², and the anode load of self-made catalysts and commercial catalysts is fixed at 0.1 mg_{Pt} cm⁻². For all the MEAs, commercial Pt/C catalysts were used as cathode, with loading controlled at 0.2 mg_{Pt} cm⁻². Then, the catalysts coated membrane and gas diffusion layer (GDL, GDS-3260) were assembled in a standard test unit (2 × 2 cm², Scribner Associates Inc.). Under the condition of 80 °C and 100% relative humidity (RH), the back pressure of fuel and O₂ was kept at 200 kPa, and the gas flow rate was controlled at 300 mL min⁻¹. And the H₂/Air PEMFC performance was test under the condition of 80°C, H₂/Air (300/300 mL min⁻¹) with normal pressure and 100% RH. After H₂-O₂ fuel cell stability test at 0.65 V for 100 h, the MEA was quenched by liquid nitrogen to obtain the cross-section. And SEM image and Energy Dispersive Spectroscopy (EDS) was used to characterize the cross-sectional structure to analyze the change in the structure of the MEA. Besides, the catalyst was scraped off from the MEA after stability test and analyzed by TEM, XRD, XPS.

1.6 Electron transfer number

Electron transfer number was determined by the Koutchy-Levich equation given below at several rotation rate:

$$J_L = 0.2nFC_0\omega^{1/2}(D_0)^{2/3}\nu^{-1/6} \quad (1)$$

Where J_L is the diffusion-limited current density, ω is the electrode rotation rate (200, 400, 900, 1600, 2500 rpm), n is the electron transfer number, F is Faraday constant (96.485 C mol⁻¹), C_0 is the bulk concentration, D_0 is the diffusion coefficient, and ν is the dynamic viscosity of the electrolyte.

1.7 DFT calculations

All structure optimization and energy calculations were performed using PBE function of the PAW potentials within the Vienna ab initio simulation package (VASP) code. The energy kinetic cut-off of plane-wave basis functions was 400 eV. A Monkhorst-Pack exchange-correlation functional with a Monkhorst-Pack grid of size 2*2*1 was used to sample the surface Brillouin zone. The electron occupancies were determined using Gaussian broadening with a width of 0.05 eV. Geometries were optimized until the energy was converged to 1.0×10^{-5} eV/atom and the force was converged to 0.05 eV/Å. A vacuum space of 15 Å was inserted in the z direction to prevent any artificial interaction between periodically repeated images under periodic boundary conditions.

Based on the EXAFS spectrum and Cs-STEM image, a small Pt₄ cluster was constructed to be anchored to the carbon substrate, which was confirmed to be the thermodynamically stable structures²⁻⁶. In order to confirm the effect of Pt₄ cluster than other larger cluster, clusters with Pt₇ and Pt₁₃ were investigated for HOR and ORR process. The reaction mechanism for HOR in acid media is as followed:



The reaction mechanism for ORR in acid media is as followed:

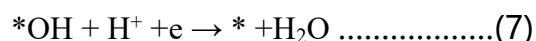
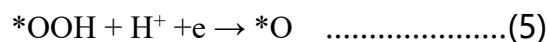


Table S1 Weight percentages determined from the ICP-MS analyses of Pt samples with different dosages.

catalysts	Pt (wt%)
Pt-C-AA-1.0%	1.038
Pt-C-AA-1.5%	1.259
Pt-C-AA-2.0%	1.531
Pt-C-AA-2.5%	1.694
Pt-C-AA-3.0%	1.680
Pt-C-AA-3.5%	1.621

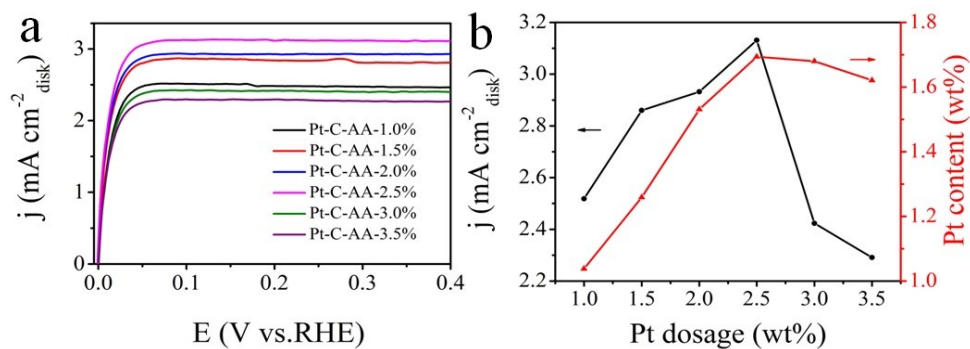


Fig. S1 (a) LSV curves of Pt-C-AA-x% with different Pt feeding ratios at pyrolysis temperature of 300 °C; (b) Dependence of current density (left) and final Pt content from the ICP-MS analyses (right) on Pt feeding amount in different Pt_x-C-AA catalysts. All these tests were done in O₂-saturated 0.1 M HClO₄ with scan rate 5 mV s⁻¹ and rotational rate 1600 rpm.

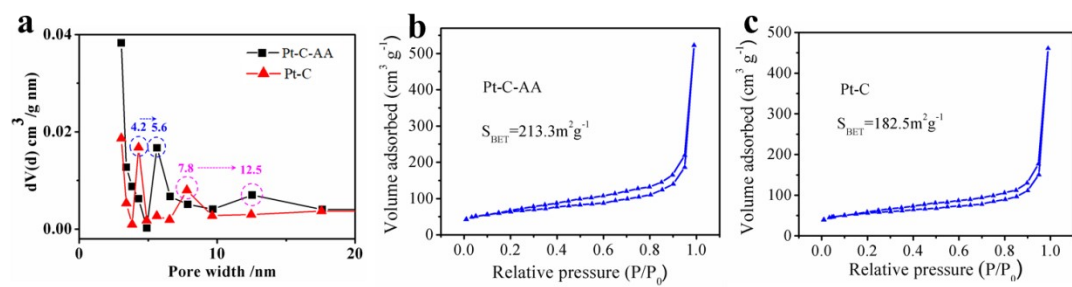


Fig. S2 The pore size distribution for Pt-C-AA and Pt-C catalysts (a); N_2 absorption and desorption isotherms plots of Pt-C-AA (b) and Pt-C (c).

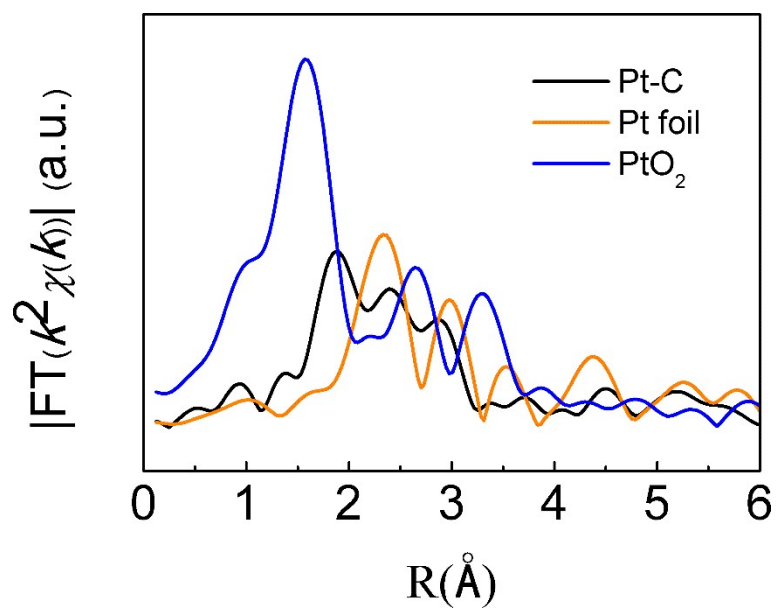


Fig. S3 The EXAFS spectrum of Pt-C, Pt foil and PtO₂.

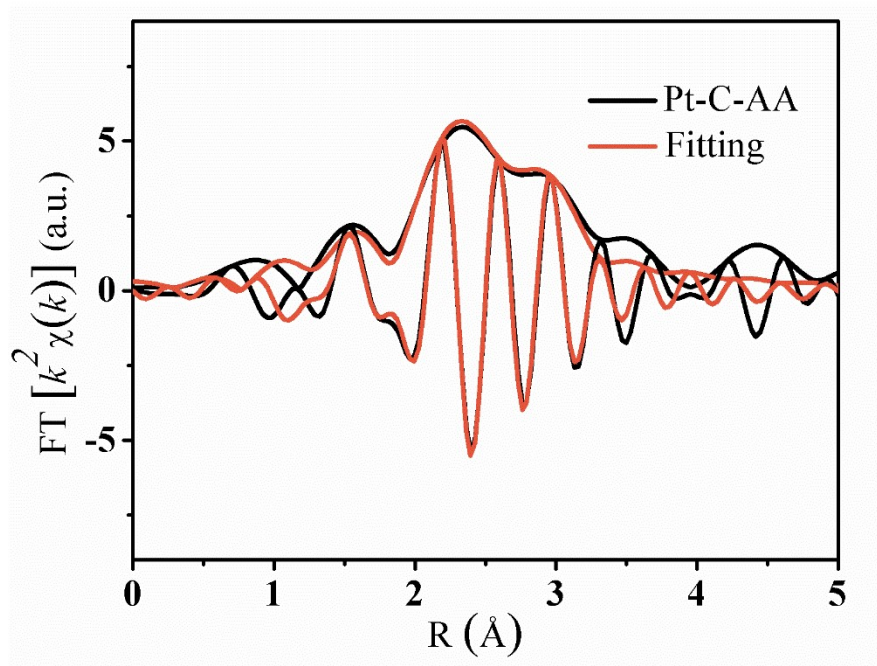


Fig. S4 EXAFS fitting results of Pt-C-AA at the R-space.

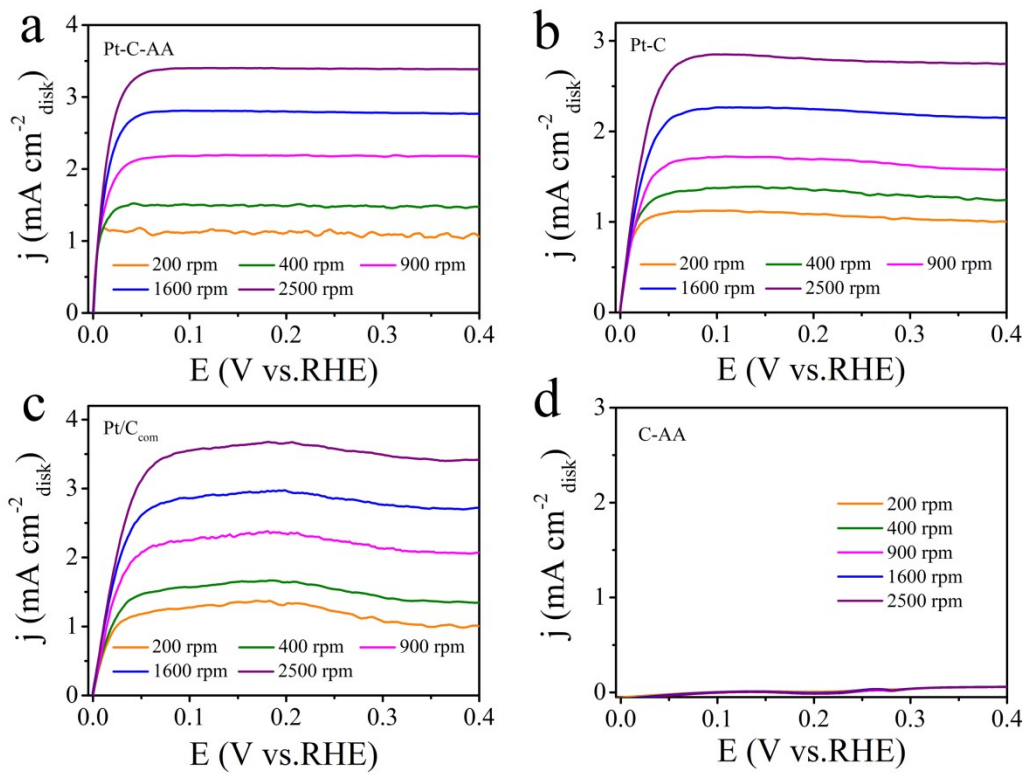


Fig. S5 The HOR behavior of the catalysts: (a) Pt-C-AA, (b) Pt-C, (c) Pt/C_{com} and (d) C-AA in 0.1 M HClO₄ H₂-saturated solution at a scan rate of 5 mV s⁻¹.

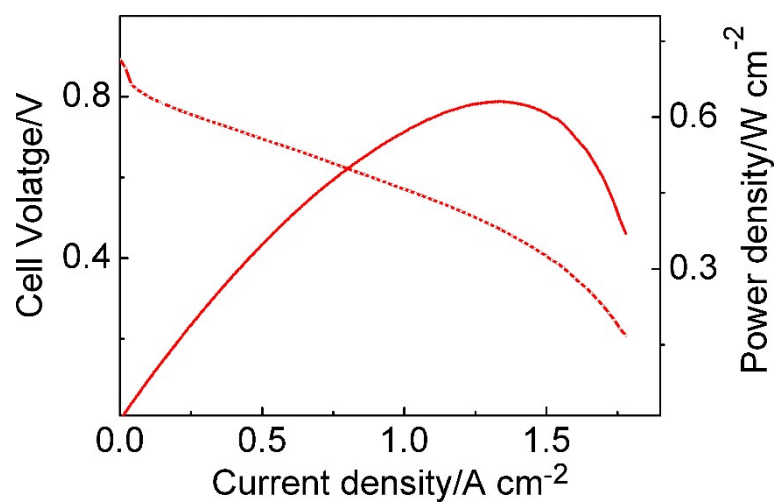


Fig. S6 H₂-Air PEMFC cell performance of the optimized anode catalysts at 80°C with normal pressure and 100% RH with Pt-C-AA as anode catalyst (0.1 mg_{Pt} cm⁻²) and commercial Pt/C as cathode catalyst(0.2 mg_{Pt} cm⁻²).

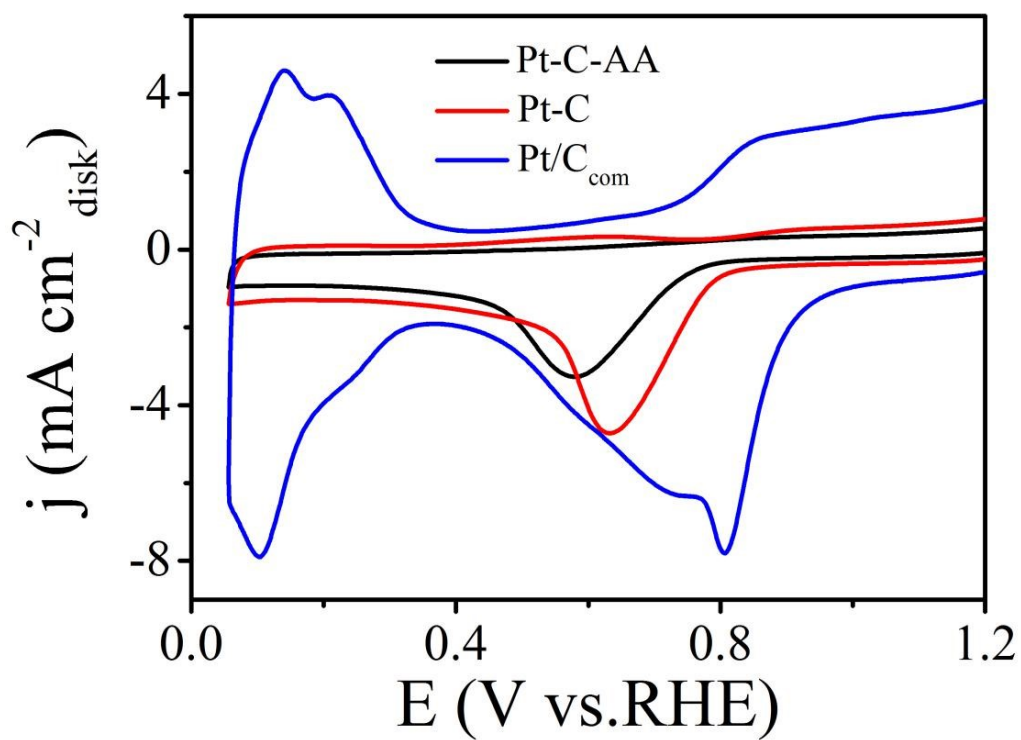


Fig. S7 CV curves of the different catalysts in O_2 -saturated 0.1 M HClO_4 solution at a scan rate of 50 mV s^{-1} .

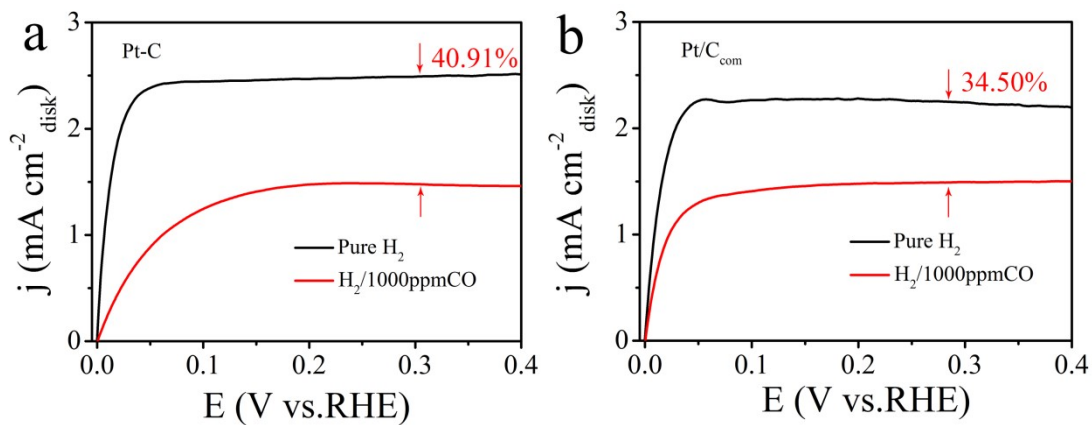


Fig. S8 The polarization curves of the (a) Pt-C and (b) Pt/C_{com} catalysts in H₂/1000 ppm CO-saturated 0.1 M HClO₄ at a scan rate of 5 mV s⁻¹ and rotation speed of 1600 rpm.

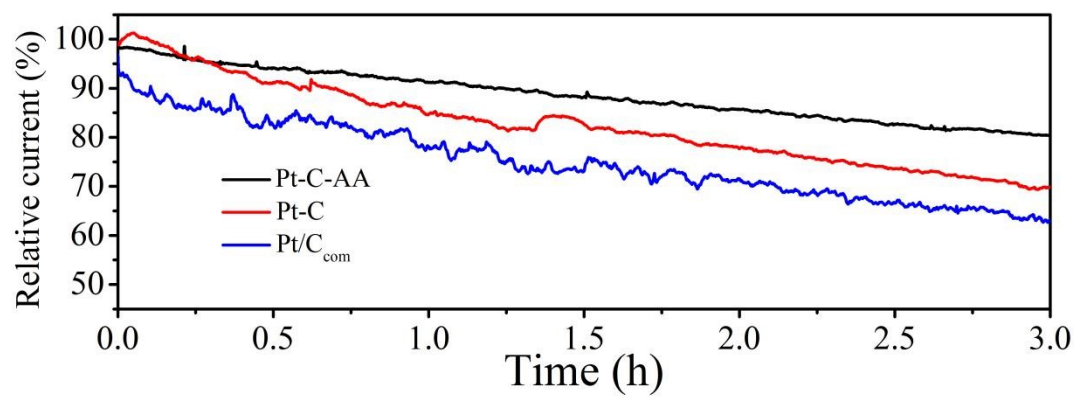


Fig. S9 Relative current-time chronoamperometry response of the different catalysts in an H₂-saturated 0.1 M HClO₄ solution at 0.1 V operated on an RDE.

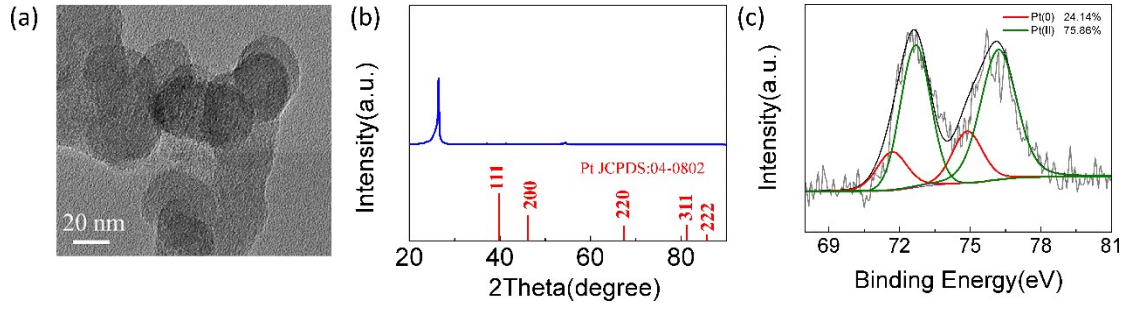


Fig. S10 (a) TEM, (b) XRD and (c) XPS spectra of Pt-C-AA after H₂-O₂ fuel cell stability test at 0.65 V for 100 h.

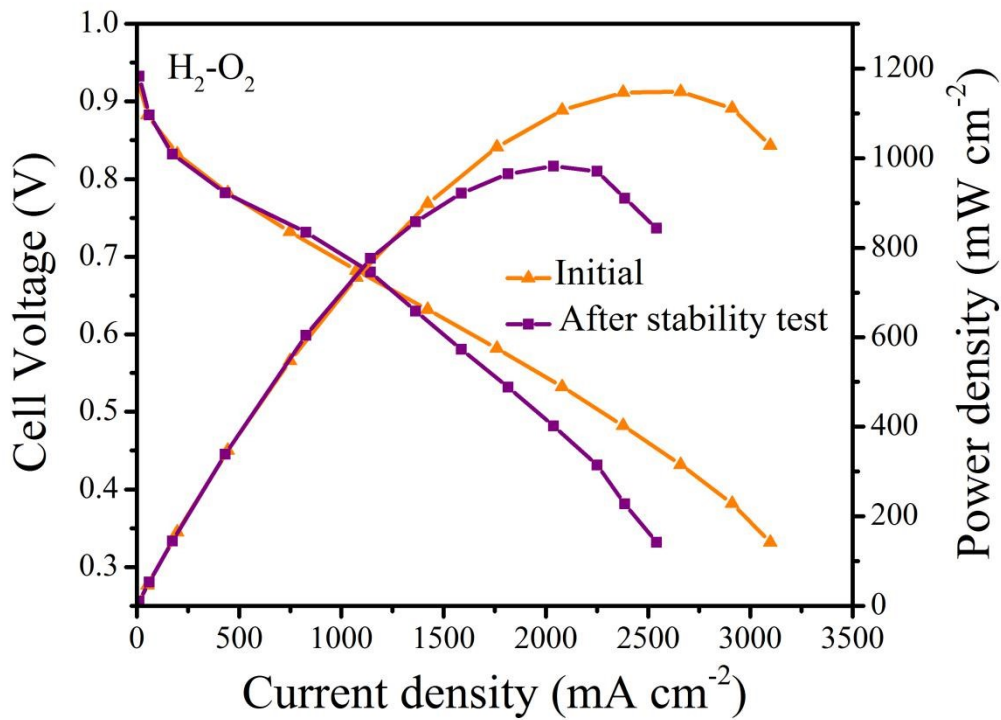


Fig. S11 H₂-O₂ PEMFC of Pt-C-AA catalyst before/after potential cycles at 80 °C with 200 kPa back pressure and 100% RH with Pt loading 0.1 mg cm⁻².

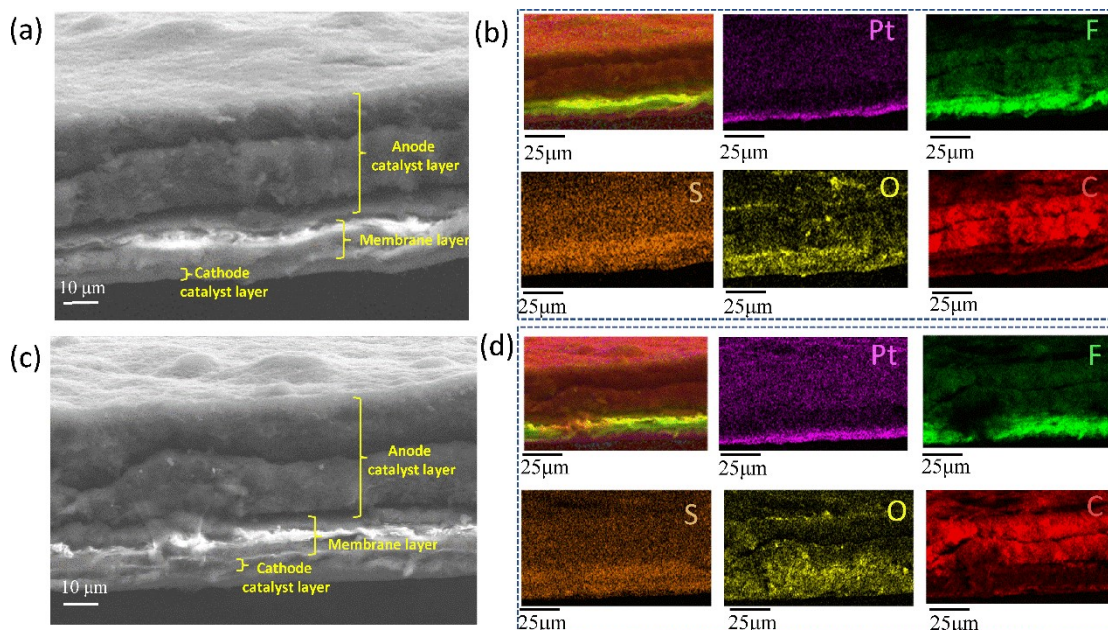


Fig. S12 Cross-sectional SEM of MEA with Pt-C-AA as anode catalyst and corresponding Energy Dispersive Spectroscopy (EDS). (a-b) before stability test, (c-d) after constant voltage mode at 0.65 V for 100h.

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