

Electronic Supplementary Information

Strengthening Pt/WO_x interfacial interactions to increase the CO tolerance of Pt for hydrogen oxidation reaction

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Experimental Section

Materials: Tungsten trioxide (WO₃ AR), Tetrammineplatinum (II) chloride, Tris(hydroxymethyl)aminomethane (C₄H₁₁NO₃ 98%), Dopamine hydrochloride (C₈H₁₁NO·2HCl 98%), ethanol (AR), Perchloric acid (HClO₄ AR).

Equipment: magnetic stirrer (Shanghai Meiyongpuyi instrument manufacturing Co., Ltd), vacuum drying oven (Shanghai Qixin science instrument Co., Ltd), vacuum pump (Chongqing Dongyue instrument Co., Ltd), high temperature tube furnace OTF-1200X (Hefei Kejing group).

Synthesis of WO_x@Pt-NC and reference samples

Firstly, tris-HCl solution (50 mM, pH≈8.5, C₄H₁₁NO₃, 99.5%) was prepared. Then, 200 mg nano-WO₃ and 60 mg dopamine were added to 20 mL tris-HCl solution in a clean beaker. The mixture was sonicated at room temperature for 1h to achieve a homogeneous dispersion. The suspension was stirred for 12 h at room temperature and then 2 mL of 0.12 M Pt(NH₃)₄Cl₂ solution was added to the beaker and stirred for another 12 h. The WO₃@PDA@Pt²⁺ was collected by centrifugation and washed with deionized water by vacuum filtration device, and then dried at 80 °C for 6 h. For the pyrolysis of WO₃@PDA@Pt²⁺, the solid powder was heated at a rate of 5 °C min⁻¹ to 700 °C in a tube furnace and the temperature was maintained for 2 h under blowing 10% H₂/90% N₂. After cooling down the sample to room temperature, the resulting product was washed with deionized water and finally dried under vacuum at 60 °C for 12 h. To determine the amount of Pt in Pt/WO_x@NC, the sample was digested in aqua regia and then analyzed by inductively coupled plasma mass spectrometry (Thermo Fisher Scientific, iCAP6300 ICP-MS). The amount of Pt was 18.5 wt%.

Sample Pt₂/WO_x@NC only doubled the Pt loading, and the rest of the preparation procedure was the same as that of Pt/WO_x@NC. Sample Pt/WO_x@NC-2 only changed the H₂/N₂ ratio (8:2) ratio during the high-temperature treatment, and the rest of the preparation procedure was the same as that of Pt/WO_x@NC. The contrast sample of Pt/WO_x-700 was prepared by the same synthesis route as that of WO_x@Pt-NC, but without the addition of dopamine.

The WO_x powder for the preparation of Pt/WO_x-gly was obtained by H₂ reduction of WO₃ under the same condition as the preparation of WO_x@Pt-NC. And the contrast samples of Pt/WO₃-gly and Pt/WO_x-gly were prepared by the glycol reduction method to reduce Pt(NH₃)₄Cl₂ on WO₃ and WO_x, respectively. Specifically, 200 mg of nano-WO₃ or WO_x was dispersed in 20 mL of glycol, then 2 mL of 0.12 M Pt(NH₃)₄Cl₂

solution was added to the mixture, followed by ultrasonic stirring for 30 min. The uniform mixture was transferred to a ground bottom flask and treated with oil bath under 160 °C for 2h. After cooling to room temperature, the resulting products were washed with deionized water and finally dried under vacuum at 60°C for 12h.

Characterization

X-ray diffraction data were collected on a Shimadzu X-ray diffractometer (model 6000) using Cu K α radiation at a step rate of 5°/min. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) observations were carried out on FEI Tecnai F20 operated at an acceleration voltage of 200 kV. Electron paramagnetic resonance (EPR) spectra were recorded on an EMXplus-6/1 BRUKER spectrometer in the X-band ($\nu_{mw} = 9.84$ GHz). The metal content of the catalysts was determined by utilizing ICP-OES (Thermo Fisher iCAP6300). X-ray photoelectron spectroscopy (XPS) analysis was performed using Thermo Scientific K-Alpha. The C 1s peak (284.8 eV) was used as the reference standard.

Electrochemical measurements

All electrochemical tests were performed by employing a Princeton electrochemical workstation (Versa STAT 4) in a 3-electrode cell with a glassy carbon rotating disk (working electrode), carbon rod (counter electrode), and Ag/AgCl (reference electrode). Before each measurement, the potential of the Ag/AgCl electrode was calibrated and then converted to a reversible hydrogen electrode (RHE). Two milligrams of catalyst powder was dispersed in a mixture of 10 μ L Nafion (5 wt%) and 800 μ L ethanol, and then the mixture was sonicated for 0.5 h to obtain the catalyst ink. Subsequently, 10 μ L catalyst ink was deposited on the working electrode. The Pt loadings of WO_x@Pt-NC, commercial Pt/C and PtRu/C on the working electrode were 23.6 μ g/cm², 25.5 μ g/cm² and 25.5 μ g/cm², respectively (determined by ICP-OES).

Cyclic voltammetry (CV) was performed in N₂-saturated 0.1 M HClO₄ electrolyte at a scan rate of 50 mV/s between 0.0 and 1.2 V for 50 cycles to remove surface contamination. The CO stripping tests were conducted in N₂-saturated 0.1 M HClO₄ electrolyte at a sweep speed of 10 mV/s between 0.0 and 1.2 V after holding potential at 0.1 V for 10 min in CO-saturated 0.1 M HClO₄ electrolyte. Linear-sweep voltammetry (LSV) technology was used to investigate the HOR activity of these catalysts in H₂-saturated 0.1 M HClO₄ electrolyte at a sweep rate of 10 mV/s between -0.05 and 0.5 V at 25 °C with rotation at 1600 rpm.

The specific kinetic current densities (J_k) associated with the intrinsic activity of catalysts were calculated by the following equation:

$$J_k = \frac{J^* J_D}{J_D - J}$$

Where J is the measured current density at 0.02 V (vs. RHE), J_D is the diffusion-limited current density, respectively.

The mass activity is calculated by the following equation:

$$MA = \frac{J_K * 0.19625}{[Pt]}$$

Where the constant 0.19625 is the area of working electrode, [Pt] is the mass of Pt on the working electrode.

MEA preparation and fuel cell testing

A certain amount of catalyst powder was dispersed in a mixture of isopropanol and Nafion solution (5 wt%), and then ultrasonicated for 0.5 h to obtain catalyst ink. Subsequently, the catalyst ink was sprayed onto Nafion HP membrane with an airbrush to form a uniform catalyst layer. The membrane was then sandwiched between two pieces of carbon paper and heat pressed at 135 °C. The Pt loading for WO_x@Pt-NC (anode) and commercial Pt/C (contrast anode and cathode) was both 0.1 mg_{Pt}/cm².

During the H₂-O₂ fuel cell tests, hydrogen (250 sccm) and oxygen (350 sccm) at 100% relative humidity were supplied to the cathode and anode. And the CO-tolerant tests for JM PtC and WO_x@Pt-NC were fed with 100 ppm CO/H₂ and 1,000 ppm CO/H₂ respectively. The fuel cell tests were operated at 80 °C with a 150 kPa backpressure at both the anode and cathode.

Figures and table

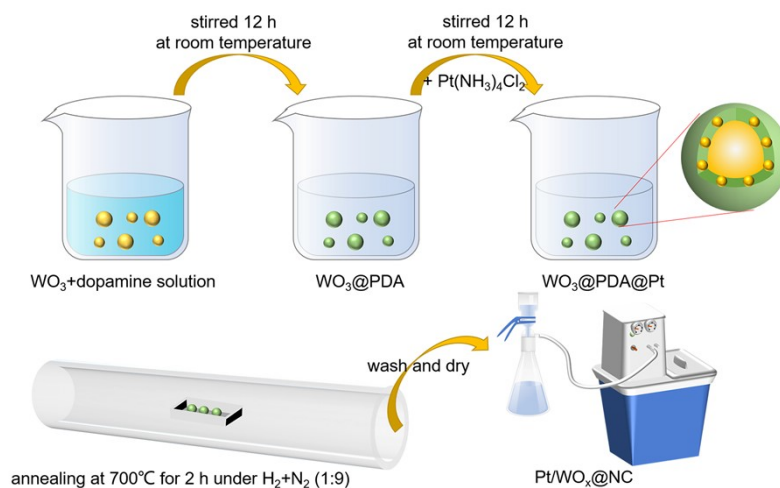


Figure S1. Synthesis scheme for Pt/WO_x@NC.

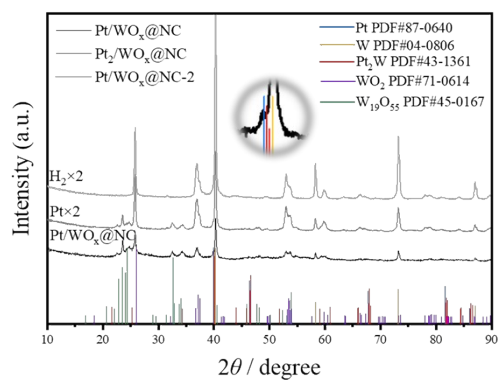


Figure S2. The XRD patterns of Pt/WO_x@NC and reference samples.

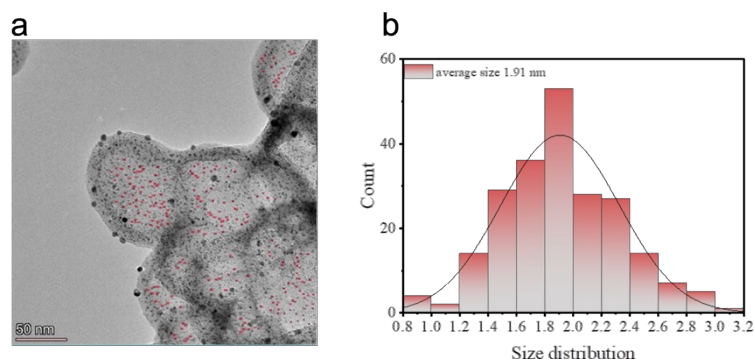


Figure S3. TEM image of Pt/WO_x@NC (a) and corresponding size distribution of Pt NPs (b).

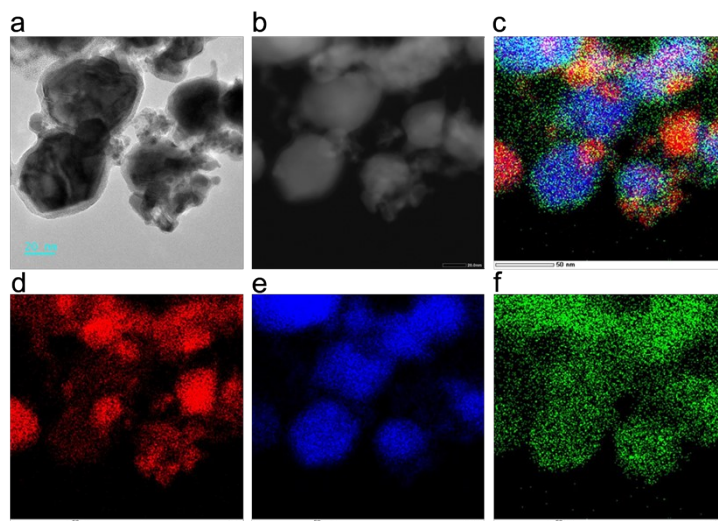


Figure S4. TEM image for Pt/WO_x-700 and corresponding EDX elemental mappings.

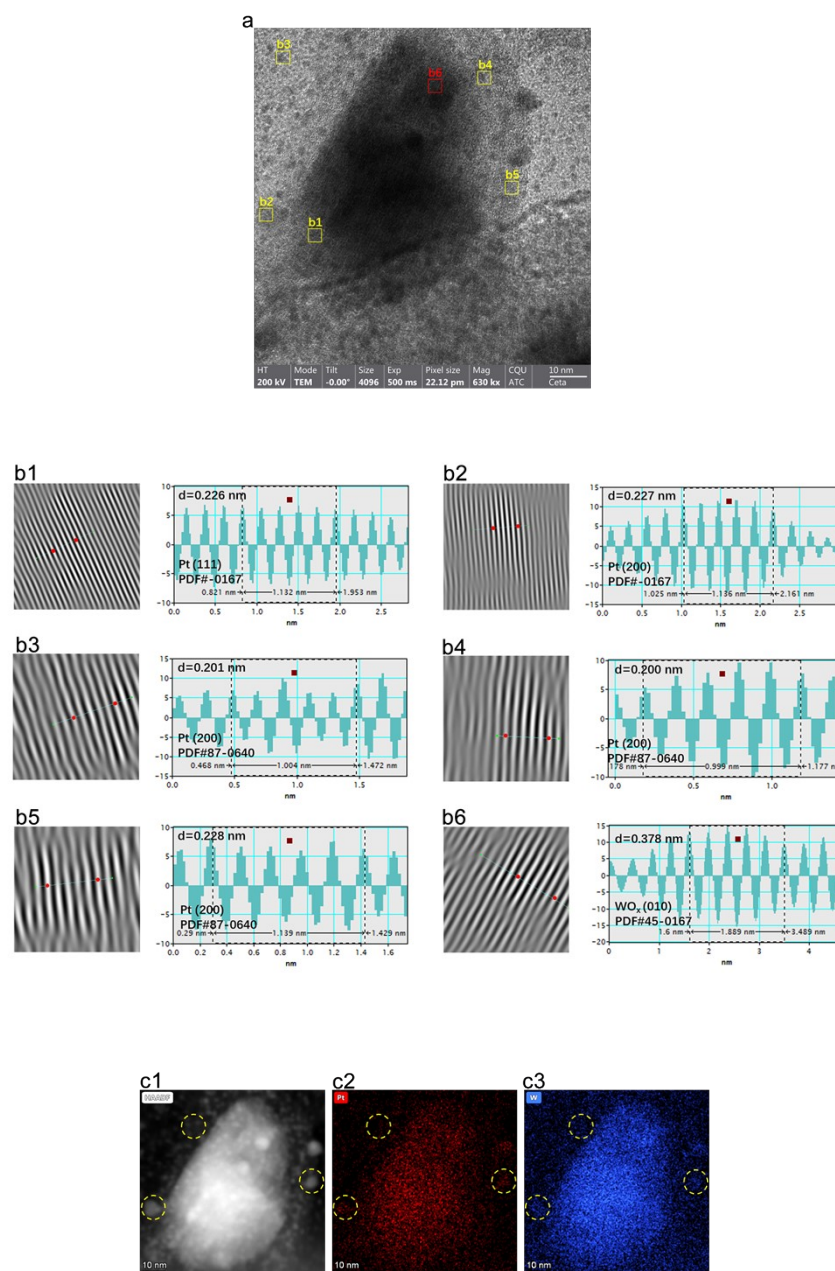


Figure S5. (a) HRTEM image for Pt/WO_x@NC. The area highlighted by the yellow box is considered to be the Pt lattice fringe (PDF#87-0640). The area highlighted by the red box is considered to be the WO_x lattice fringe (PDF#45-0167). (b) The measured lattice spacings for Pt (b1-b5) and WO_x (b6) in Fig. S5a. The left images have been Fourier transformed. (c) The corresponding HAADF image and EDX mappings of Fig. S5a.

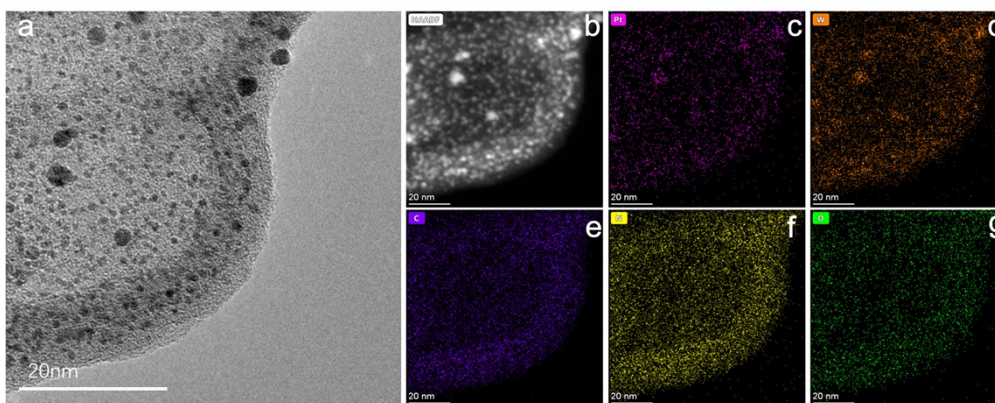


Figure S6. TEM image for Pt/WO_x@NC and corresponding EDX elemental mappings.

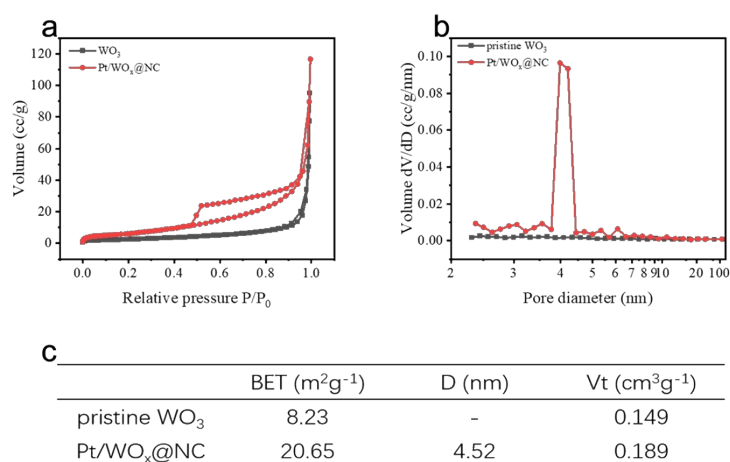


Figure S7. (a-b) N₂ adsorption–desorption isotherms (a) and pore-size distribution plots (b). (c) The pore parameters of WO₃ and Pt/WO_x@NC.

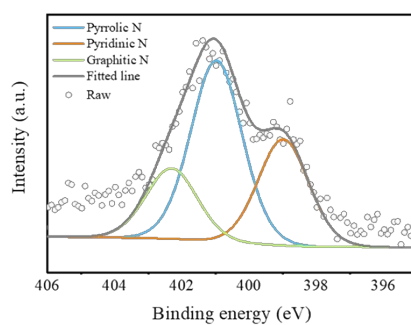


Figure S8. High-resolution XPS spectrum for N 1s in Pt/WO_x@NC.

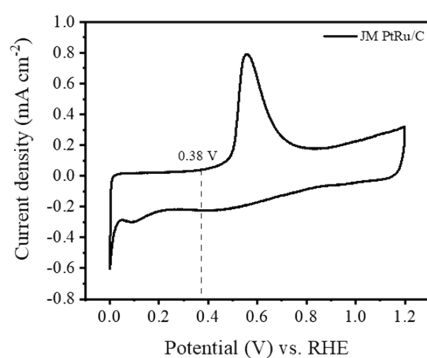


Figure S9. The CO stripping curve of JM PtRu/C.

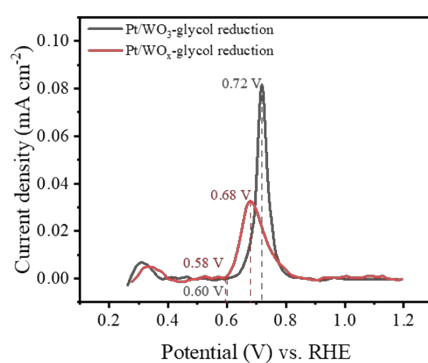


Figure S10. The CO stripping curves for Pt/WO_x-gly and Pt/WO₃-gly respectively.

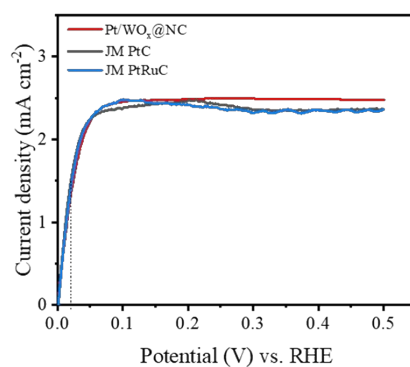


Figure S11. The HOR curves for Pt/WO_x@NC, JM PtRu/C and JM Pt/C respectively.

Table S1. A brief comparison of the CO oxidation potential of catalysts recently

reported in the literature with the home-made WO_x@Pt-NC.

Catalysts	On set potential of CO oxidation	Experiment condition	Ref
PtRu@h-BN/C	0.50 V vs. RHE	25°C, 0.1M HClO ₄ , 20 mV/s	1
Pt/C+WO _x	0.60 V vs. RHE	25°C, 0.1M HClO ₄ , 50 mV/s	2
NPG-Pt ₁ Ru ₁	0.42 V vs. RHE	25°C, 0.5M H ₂ SO ₄ , 20 mV/s	3
Pt/TiWN/C	0.56 V vs. RHE	25°C, 0.1M HClO ₄ , 50 mV/s	4
Pt/C-RuO _x Hy	0.55 V vs. RHE	25°C, 0.5M HClO ₄ , 20 mV/s	5
PtRu/W _x CyO _z	0.48 V vs. RHE	25°C, 0.5M HClO ₄ , 100 mV/s	6
Pt _{2AL} -PtFe/C	0.56 V vs. RHE	70°C, 0.1M HClO ₄ , 20 mV/s	7
WO _x @Pt-NC	0.24 V vs. RHE	25°C, 0.1M HClO ₄ , 10 mV/s	This work

Reference

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