Supporting Information

High Temperature Self-assembly One-step Synthesis of Structurally

Ordered PtFe catalyst for Oxygen Reduction Reaction

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1. Experimental

Synthesis of Ordered PtFe Intermetallic Catalyst: Typically, 80 mg of Vulcan XC-72 carbon support (Cabot) was added to 60 mL of mixture solution of ethanol and deionized water (V:V=1:1), then stirred ultrasonically for 2 h to obtain a homogeneous solution. Next, 10 mL of Tris-HCl buffer solution (50 mM, pH≈8.5) with 60 mg of dopamine was added into the above mixture solution. Then, polydopamine (PDA) was selectively coated onto carbon surface (C@PDA) after stirring for 24 h at room temperature, which was collected by filtrating and washing with deionized water for several times. After that, the C@PDA was re-dispersed in 30mL of deionized water with 0.102 mmol Pt(NH₃)₄Cl₂ and 0.306 mmol FeNO₃ precursors and stirred for 24 h to obtain the composites of $Pt(NH_3)_4^{2+}$ and Fe^{3+} adsorption (C@PDA-Pt(NH_3)_4^{2+}-Fe^{3+}). After stirring, 3 mL of HCl (pH=3), 3 mL of Tetraethyl orthosilicate (TEOS) and 5 mL of ethanol were added. Next, the mixture was stirred at room temperature for 1 h. The mixture was then poured into glass petri dishes and made slowly evaporated under ambient conditions until solid films (C@PDA-Pt(NH₃)₄²⁺-Fe³⁺@SiO₂) formed. Then thermal annealing, the C@PDA-Pt(NH₃)₄²⁺-Fe³⁺@SiO₂ was heated to 120°C for 2 h with a rate of 5°C min⁻¹ under flowing 10% $H_2/90\%$ N₂ atmosphere, then increased to 800°C for 2 h, lastly, cooled to room temperature. The crude fct-PtFe/C@NC@SiO₂ composite was etched by 10% HF followed by 2 mol/L NaOH to remove the silica layers and unstable Fe species. After etching, the sample was filtered and washed several times with alcohol and deionized water, and then dried

in vacuum oven (60°C) for 8 h.

For comparison, the sample of Pt/C@NC was prepared under similar conditions to that of fct-PtFe/C@NC without using Fe precursor.

2. Electrochemical measurements

All electrochemical analysis were carried out using a Princeton electrochemical workstation (VersaSTAT 3, AMETEK) equipped with a Pine rotational disk electrode (RDE) in a conventional three-electrode cell at room temperature. A modified glassy carbon electrode (GC, area 0.19625 cm², PINE: AFE3T050GC), an Ag/AgCl (3M KCl) electrode and a high purity graphite rod were used as working, reference and counter electrodes, respectively. All measured potentials were converted to values relative to the reversible hydrogen electrode (vs. RHE) by calibration in a H₂-saturated 0.1 M HClO₄ solution.

The working electrodes were prepared as follows: the catalyst was dispersed in mixture of ethanol and 5µL of Nafion solution (5 wt. %) under ultrasonic agitation for 30 minutes to form uniform ink. Then, 10 µL of the well-dispersed catalyst ink was deposited on a pre-polished GC disk. The total Pt loading were calculated to be 0.15 mg cm⁻² and 0.25 mg cm⁻² for fct-PtFe/C@NC and the commercial Pt/C catalysts, respectively.

Cyclic voltammetry (CV) was carried out in N₂-saturated 0.1 M HClO₄ solution at potential sweep from 0.04 to 1.2 V (vs. RHE) at a sweep rate of 50 mV s⁻¹ for 70 cycles. Electrochemical active surface area (ECSA) were estimated by integrating the charge associated with CO stripping peak and the hydrogen adsorption between 0.05 and 0.40 V. The oxygen reduction reaction ORR polarization curves were conducted by linear sweep voltammetry (LSV) curves in O_2 -saturated 0.1 M HClO₄ solution which was purged with O_2 during the measurement. The LSV curves was recorded at potential sweep from 0 to 1.1 V (vs. RHE) at rotation speed of 1600 rpm and the scan rate of 10 mV s⁻¹ with ohmic IR drop compensation. After the ORR measurements, CO gas was bubbled into the HClO₄ solution approximately for 20 minutes and then CO Stripping measurement was obtained at a sweep rate of 50 mV s⁻¹ in fresh 0.1 M HClO₄ solution which was purged with N₂ during the measurement. The accelerated durability test (ADT) was examined at room temperature in O_2 -saturated 0.1 M HClO₄ solution by applying cyclic potential sweeps between 0.6 and 1.1 V at a sweep rate of 50 mV s⁻¹ for 30,000 CV cycles. The electrochemical surface area (ECSA) of Pt in the catalysts were estimated by the following equation (1), (2):

$$ECSA - H_{upd} = \frac{Q_H}{0.21mC/cm^2 * [Pt]}$$
(1)

$$ECSA_{CQ} = \frac{Q_{CO}}{0.42mC/cm^2 * [Pt]}$$
(2)

where Q_H (mC) is the charge measuring the hydrogen adsorption/desorption between 0.05 and 0.40 V of the CVs, 0.21 mC cm⁻² is the electrical charge of monolayer adsorption of hydrogen on Pt, where Q_{CO} (mC) is the charge obtained by integrating CO stripping peak area, 0.42 mC cm⁻² is the electrical charge associated with monolayer adsorption of CO on Pt, and [Pt] (m² g⁻¹) is the mass of Pt on the working electrode.

The specific kinetic current densities (J_K) associated with the intrinsic activity of catalysts was calculated by the following equation (3):

$$J_K = \frac{J * J_D}{J_D - J} \tag{3}$$

Where J_K is the kinetic current density, J is the measured current density at 0.9 V (vs. RHE), J_D is the diffusion-limited current density, respectively.

3. Characterization

The morphology and particle size distribution of the fct-PtFe/C@NC catalyst was characterized by transmission electron microscopy (TEM, Zeiss LIBRA 200 FETEM, 120 kV). The composition and atomic distribution of PtFe nanoparticles were analyzed by high-resolution transmission electron microscopy (HRTEM, JEM-2100, 200 kV) and high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) with energy-dispersive X-ray spectroscopy (EDX, Aztec X-Max 80 TEM, 200 kV). The crystalline structure was characterized by X-ray powder diffraction (XRD) conducted on a PANalytical X' pert diffractometer at 30 kV with Cu K α radiation at a step rate of 5° min⁻¹. X-ray Photoelectron Spectroscopy (XPS) measurement was operated at an ESCALAB250Xi spectrometer with a monochromatic Al X-ray source (Al K α , 1.4866 keV), the binding energies were calibrated for catalysts charging by referencing C 1s (284.8 eV). The compositional contents of samples was obtained by the inductively coupled plasma mass spectrometery (ICP-MS, Thermo Fisher Scientific, iCAP6300).

4. Additional figures and tables



Fig.S1 TEM images and particle distribution histograms of fct-PtFe/C@NC catalyst, (a) bright field image, (b) dark field image.



Fig.S2 HAADF-STEM image of an ordered PtFe nanoparticle and corresponding EDX line-scanning profile.



Fig.S3 (a) XPS surveys of JM-Pt/C and fct-PtFe/C@NC catalysts; (b) the high resolution Fe 2p spectra of fct-PtFe/C@NC catalyst.



Fig. S4 (a) CV curves of ordered fct-PtFe/C@NC and JM-Pt/C catalysts recorded in N_2 -purged 0.1 M HClO₄ solution at a scan rate of 50 mV s⁻¹. (b) The CO stripping images of fct-PtFe/C@NC and JM-Pt/C catalysts.



Fig.S5 (a) CV curves of JM-Pt/C, Pt/C@NC and fct-PtFe/C@NC catalysts recorded in N₂-purged 0.1 M HClO₄ solution at a scan rate of 50 mV s⁻¹. (b) ORR polarization curves of JM-Pt/C, Pt/C@NC and fct-PtFe/C@NC catalysts in O₂ saturated 0.1 M HClO₄ at 10 mV s⁻¹ and a rotating speed of 1600 r pm.



Fig. S6 CV curves of ordered fct-PtFe/C@NC (a) and JM-Pt/C (b) catalysts before and after 30,000 cycles potential between 0.6 and 1.1 V versus RHE, recorded in O_2 -saturated 0.1 M HClO₄ solution at a scan rate of 50 mV s⁻¹.



Fig.S7 TEM images and particles size distribution of fct-PtFe/C@NC catalyst before (a, a*) and after ADT (b, b*), JM-Pt/C catalyst before (c, c*) and after ADT (d, d*).



Fig. S8 (a) CV curves of ordered Pt/C@NC catalyst before and after 30,000 cycles potential between 0.6 and 1.1 V versus RHE, recorded in O_2 - saturated 0.1 M HClO₄ solution at a scan rate of 50 mV s⁻¹. (b) ORR polarization curves of Pt/C@NC catalyst before and after 30,000 potential cycles with a sweep rate of 10 mV s⁻¹ and a rotation rate of 1600 rpm.



Fig. S9 Raman spectrum of JM-Pt/C and fct-PtFe/C@NC catalysts.

Commis -	Elemental contents (wt.%)					
Sample –	C 0	0	Ν	Fe	Pt	
fct-PtFe/C@NC	86.61	10.93	1.32	0.46	0.68	
JM-Pt/C	92.06	4.31	_	_	3.63	

 Table S1 Comparison of surface elemental contents of fct-PtFe/C@NC and JM-Pt/C catalysts obtained from XPS measurements.

Sample	E _{1/2} IR-free (V)	Mass activities at 0.9V (A mg ⁻¹)	Specific activity (mA cm ⁻²)	ECSA (m ² g ⁻¹)
JM-Pt/C	0.887	0.210	0.290	71
fct -PtFe/C@NC	0.918	0.769	1.17	65
Pt/C@NC	0.904	0.248	0.393	63

Table S2 $E_{1/2}$, mass activity, Specific activity and ECSA at 0.9 V versus reversiblehydrogen electrode for JM-Pt/C, fct-PtFe/C@NC and Pt/C@NC catalysts.

	Mass activities at 0.9V (A mg ⁻¹)	Specific activity (mA cm ⁻²)	ref
ordered PtFe@C	~0.26	~0.37	1
fct-PtFe/C	1.6	2.3	2
Pt ₃ Fe	0.12	0.617	3
fct-FePt	0.69	3.16	4
PtFe/C	~0.216	0.514	5
Pt ₄₅ Fe ₅₅ /OMC	0.283	0.228	6
US DOE 2020 target	0.44		7
fct-PtFe/C@NC	0.769	1.17	This work

Table S3 ORR activity data of similar PtFe alloys from the previous literatures. All the potentials are referred to RHE.

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