

Supporting Information

Refined Structural Analysis of Connected Platinum–Iron Nanoparticle Catalysts with Enhanced Oxygen Reduction Activity.

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S1. Experimental Methods

Catalyst Preparation

A connected Pt–Fe nanoparticle catalyst was prepared based on our previous reports.^{1,2} The preparation procedure is briefly described below. First, Pt–Fe nanoparticles were densely covered on an amorphous spherical silica template (*ca.* 300 nm in diameter, KE-P30, Nippon Shokubai) using the polyol synthesis method. Next, the obtained Pt–Fe nanoparticles on silica were treated in supercritical ethanol at 330 °C and at *ca.* 20 MPa for ~3 h, leading to the formation of a beaded network of the fused Pt–Fe nanoparticles. Finally, by etching the silica template in an alkaline aqueous solution (3M NaOH) at 85 °C, a connected Pt–Fe nanoparticle catalyst with a porous hollow-capsule structure was obtained. The Pt:Fe atomic composition of the prepared catalyst was 49:51, which was determined using inductively coupled plasma-atomic emission spectroscopy (ICPS-8100, Shimadzu).

The uniform and thinner catalyst electrodes were prepared according to the method reported in the literature.¹ The electrochemically (EC) pretreated catalysts were then prepared using 50 cycles of cyclic voltammetry (CV) in a N₂-purged 0.1 M HClO₄ electrolyte solution at potentials ranging from 0.05 V to 1.2 V (vs. RHE) and a sweep rate of 50 mV s⁻¹. The 50 CV cycles stabilized the voltammograms, indicating the stable catalyst surface structures. This pretreatment condition was the same as that for the oxygen reduction reaction (ORR) activity tests conducted in our previous report.¹ Thus, the catalyst structures after the EC pretreatment are directly linked to their ORR activities.

Catalyst Characterizations

A refined structural analysis of the connected Pt–Fe catalysts was performed according to the following methods. The structure of a commercial Pt nanoparticle catalyst supported on carbon black (Pt/C, TEC10E50E, Tanaka Kikinzoku Kogyo) was analyzed for obtaining reference data.

The XRD data of the catalysts were collected over a 2θ range of 30° – 100° at a scan rate of $2.5^\circ \text{ min}^{-1}$ using an X-ray diffractometer (SmartLab, Rigaku) with Cu $K\alpha 1$ ($\lambda = 1.5406 \text{ \AA}$) radiation produced at 45 kV and 120 mA. The ratio of the chemically ordered fct and disordered fcc structures for the connected Pt–Fe catalysts was determined via Rietveld structure refinement of the XRD data.

Table S1. Results of Rietveld analysis for the connected Pt–Fe catalyst after the EC treatment.

	Phase	Space group	Composition (%)	Lattice constant		Unit cell volume (\AA^3)
				a (\AA)	c (\AA)	
EC-pretreated, connected Pt–Fe	fcc	Fm-3m	73	3.83	3.83	56.26
	fct	P4/mmm	27	3.84	3.68	27.17

Reliability factor: $R_{wp} = 6.39$, $S = 2.45$

Space group *Fm-3m* (No. 225)
 $a = b = c = 3.696 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$

Atoms	Site	g	x, y, z	U (\AA^2)
Pt	4a	0.52	0, 0, 0	0.063
Fe	4a	0.48	0, 0, 0	0.063

Space group $P4/mmm$ (No. 123)

$a = b = 3.817 \text{ \AA}$, $c = 3.647 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$

Atoms	Site	g	x, y, z	U (\AA^2)
Pt	1a	0.52	0, 0, 0	0.063
Fe	1a	0.48	0, 0, 0	0.063
Pt	1d	0.52	0.5, 0.5, 0.5	0.063
Fe	1d	0.48	0.5, 0.5, 0.5	0.063

In situ XAS analysis was performed using synchrotron radiation X-rays at the Pt L₃-edge and Pt L₂-edge in a transmission configuration (Beamline: BL16B2, SPring-8).³ Prior to XAS measurements, the catalyst electrodes were pretreated electrochemically via 50 cycles of CV, and the in situ XAS data were then obtained at 0.4 V vs. RHE in a 0.1 M HClO₄ electrolyte solution. EXAFS and XANES analyses were performed using the Athena and Artemis programs in the IFEFFIT package.⁴ The initial structural parameters for the EXAFS analyses were determined based on the Rietveld structure refinement results. The white line peaks of the Pt L₃- and Pt L₂-edge XANES spectra were analyzed using a procedure proposed by Mansour to estimate the Pt 5*d* vacancies in the catalysts.⁵

TEM (H-8100, Hitachi High Technologies Corporation) and Cs-corrected STEM (JEM-ARM200F, JEOL) observations for the catalysts were performed with an acceleration voltage of 200 kV. The metal profiles in the connected Pt–Fe networks were determined using the obtained STEM–EDX line-scan data.

S2. In situ XAS analysis for the EC-pretreated catalysts

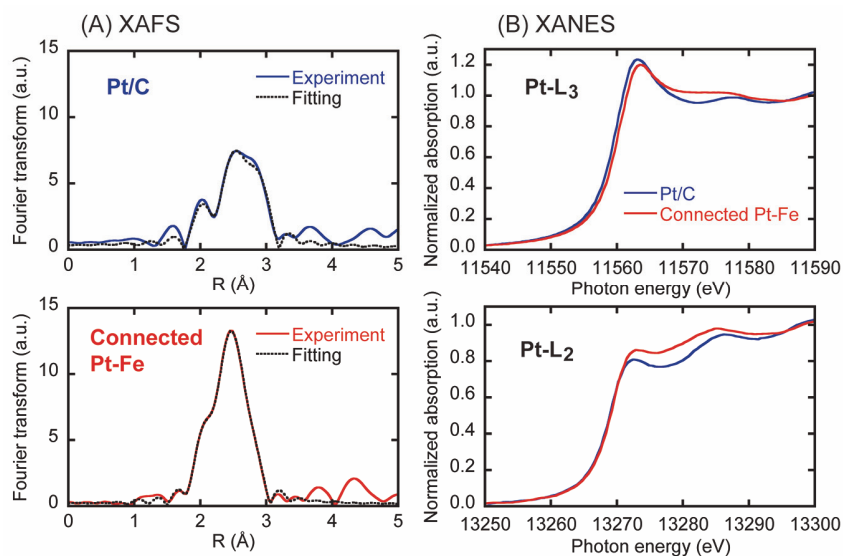


Figure S1. (A) Experimental and fitting data for the k^3 -weighted Fourier transforms of the Pt L₃-edge EXAFS spectra; (B) Pt L₃- and L₂-edge XANES spectra at a potential of 0.4 V versus reversible hydrogen electrode (vs. RHE) in a 0.1 M HClO₄ electrolyte solution; (blue) Pt/C and (red) connected Pt-Fe catalysts after the EC pretreatment.

S3. Lattice fringe spacing analysis in Pt nanoparticles

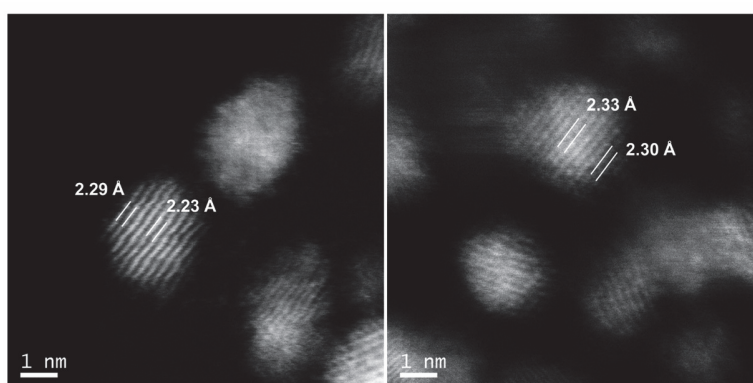


Figure S2. Cs-corrected STEM images with lattice spacings for Pt nanoparticles of the Pt/C catalyst after the EC pretreatment.

S4. Atomic stepped surface of the connected Pt–Fe catalyst

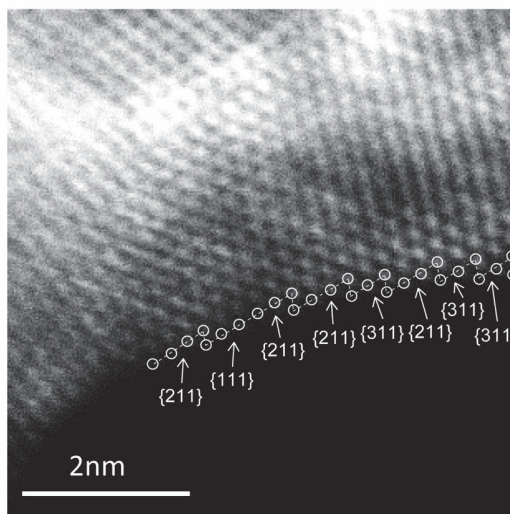


Figure S3. Cs-corrected STEM image for the facet analysis on the outermost surface of the connected Pt–Fe catalyst after the EC pretreatment.

References

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