Supporting Information

~~A~~ New Approach to Fully-Ordered fct-FePt Nanoparticles for Much Enhanced Electrocatalysis in Acid

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Experimental Section

Chemicals and Materials: Pt(acac)$_2$ (98%), Mg(acac)$_2$ (anhydrous, 98%) (acac = aceylacetonate) were purchased from Strem Chemicals. Oleylamine (70%), oleic acid (90%), 1-octadecene (90%), benzyle ether (98%), Fe(CO)$_5$, 1,2-tetradecanediol (90%) and Nafion (5% in a mixture of lower aliphatic alcohols and water) were purchased from Sigma-Aldrich. All chemicals were used without further purification. The commercial Pt catalyst (20% mass loading on carbon, Pt particle diameter at 2.5-3.5 nm) was obtained from Fuel Cell Store.

Characterization: X-ray diffraction (XRD) patterns of the NPs were collected on a Bruker AXS D8-Advanced diffractometer with Cu Kα radiation (λ = 1.5418 Å). Transmission electron microscopy (TEM) images were acquired from a Philips CM20 operating at 200 kV. High-resolution TEM (HR-TEM) images were recorded using a JEOL 2010 with an accelerating voltage of 200 kV. TEM and HR-TEM samples were prepared by depositing a single drop of diluted NPs dispersion on amorphous carbon-coated copper grids. Scanning transmission electron microscopy (STEM) analyses were carried out on a Hitachi HD2700C (200 kV) with a probe aberration corrector, at the Center for Functional Nanomaterials, Brookhaven National Lab. The electron energy loss spectroscopy (EELS) line-scan was obtained by a high-resolution Gatan-Enfina ER with a probe size of 1.3 Å. A power law function was used for EELS background subtraction. Magnetic studies were performed on a Quantum Design Superconducting Quantum Interface Device (SQUID) with a field up to 70 kOe. The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements were carried on a JY2000 Ultrace ICP atomic emission spectrometer equipped with a JY AS 421 autosampler and 2400g/mm holographic grating.

Synthesis of dumbbell fcc-FePt-Fe_3O_4 NPs: In a four-neck flask, a mixture of 0.1g $Pt(acac)_2$, 0.7 mL oleylamine, 0.65 mL oleic acid and 5 mL 1-octadecene was stirred and degassed at 120°C under an Ar atmosphere for 30 min. Under a blanket of Ar, $Fe(CO)_5$ (0.05 mL) was injected into the mixture solution. Subsequently, the temperature was raised to 220°C at a rate of 5°C/min and kept at this temperature for 30 min. Then the mixture was heated to 300°C at a rate of 10°C/min and maintained at this temperature for 10 min before cooled down to room temperature. The product was precipitated by 2-propanol and collected by centrifugation (8500 rpm, 8 min). The product was redispersed in hexane and separated by adding ethanol and centrifugation (8500 rpm, 8 min). The final product was dispersed in hexane for further use.

Synthesis of FePt-Fe_3O_4/MgO and fct-FePt/MgO NPs: A mixture of 0.4 g $Mg(acac)_2$, 0.42 g 1,2-tetradecanediol, 0.9 mL oleylamine, 0.6 mL oleic acid was dissolved in 18 mL benzyl ether under vigorously stirring and degassed at 120°C. 60 mg of the as-synthesized fcc-FePt-Fe_3O_4 NPs dispersed in 5 mL of hexane was added into the flask. The mixture was kept degassed for 20 min to remove hexane. Then under the blanket of Ar, the solution was heated up to 300°C and maintained at this temperature for 60 min before cooled down to room temperature. The product was precipitated with ethanol, centrifuged (8500 rpm, 8 min) and dried. After annealing at 700°C under Ar + 5%H_2, fct-FePt/MgO NPs were obtained.

Synthesis of carbon supported fct-FePt (C-fct-FePt) NPs: To prepare C-fct-FePt NPs, 20 mg of fct-FePt/MgO was dispersed in 20 mL ethanol under ultrasonication, and 0.6 mL of concentrated HNO_3 was then added dropwise into the dispersion. The solution was sonicated for 5 min and 10 mg Ketjen carbon power was added. The mixture was kept sonicated for 1 h. Then the C-fct-FePt NPs were separated by centrifugation and washed with ethanol and DI water. The NP/C weight ratio is ~1/2 measured by ICP-AES.

Synthesis of fcc-FePt NPs and C-fcc-FePt catalyst: In a four-neck flask, a mixture of 0.1 g $Pt(acac)_2$, 0.7 mL oleylamine, 0.65 mL oleic acid, and 5 mL 1-octadecene, was stirred and degassed at 120°C under an Ar atmosphere for 30 min. Under a blanket of Ar, 0.09 mL $Fe(CO)_5$ was injected into the mixture solution. Subsequently, the temperature was raised to 220°C at a rate of about 5°C/min and kept at this temperature for 1 h before it was cooled to room temperature. The product was precipitated by 2-propanol and collected by centrifugation (8500 rpm, 8 min). The product was redispersed in hexane and separated by adding ethanol and centrifugation (8500 rpm, 8 min). The final product was dispersed in hexane for further use. ICP-AES measurement confirmed the molar ratio of Fe/Pt to be 50/50. To load the NPs on carbon, the as-synthesized fcc-FePt NPs and Ketjen-300J carbon at a weight ratio of 1:2 were mixed in 20 mL of hexane and 10 mL of isopropanol and sonicated for 1 h. The product was separated by centrifugation. The C-fcc-FePt were dried under ambient conditions and annealed at 400°C for 1 h in a gas flow of Ar + 5% H_2 to remove the surfactant.

Electrochemical Measurements: Electrochemical measurements were performed on an Autolab 302 potentiostat with glassy carbon rotating disk (5 mm in diameter) as a working electrode, Ag/AgCl (4 M KCl) as a reference electrode, and platinum wire as a counter electrode. The potential difference between Ag/AgCl and RHE was measured in H_2 saturated 0.1 M $HClO_4$ electrolyte and the value is 0.260 ± 0.001 V. All potentials were later converted to the RHE scale. All catalysts were dispersed in a mixture containing water, isopropanol, and Nafion (5%) (v/v/v 4:1:0.05) to form a 2 mg/mL ink. 20 µL of catalyst ink was casted on the newly polished glassy carbon electrode and dried at ambient condition. The Pt loadings of fully-ordered fct-FePt, partially-ordered fct-FePt, fcc-FePt and commercial Pt were calculated to be 45.5, 47.1, 37.6 and 40 $\mu g_{Pt}/cm^2$, respectively. The catalysts were first subject to cyclic voltammetry (CV) scans between 0.05 and 1.3 V at 100 mV/s in N_2-saturated 0.1 M $HClO_4$ until a stable CV was obtained (typically 200 cycles). The ECASA was calculated by measuring the charge collected in the hydrogen adsorption/desorption regions after double-layer correction, assuming a value of 210 $\mu C/cm^2$ for the adsorption of a hydrogen monolayer on polycrystalline Pt. ORR polarization curves were recorded by linear-sweep voltammetry (LSV) at a scan rate of 10 mV/s in O_2-saturated 0.1 M $HClO_4$ with the GC-RDE rotating at 1600 rpm. The kinetic current was calculated from the ORR polarization curve according to the Koutecky–Levich equation. Accelerated durability tests (ADT) of the catalysts for ORR were conducted by cycling the potential between 0.6 and 1.0 V at 100 mV/s. To evaluate the production of H_2O_2 of fct-FePt during the ORR, rotating ring/disk electrode (RRDE) experiments were carried out with the ring potential setting to 1.2 V. The four-electron selectivity of catalysts was evaluated based on the H_2O_2 yield, calculated from the following equation:

$$\mathrm{H_2O_2}(\%) = 200 \times \frac{I_R / N}{(I_R / N) + I_D}$$

Here, I_D and I_R are the disk and ring currents, respectively, and N is the ring collection efficiency (~37%) provided by the manufacturer based on the geometry of the electrodes.

HER polarization curves were recorded by LSV at a scan rate of 2 mV/s in O_2-saturated 0.5 M H_2SO_4 without electrode rotation. Durability of catalysts for HER was conducted by cycling the potential between -0.3 and 0.9 V at 100 mV/s.

MEA Preparation and Fuel Cell Testing: The membrane electrode assemblies (MEAs) were fabricated using Nafion® 212 membrane in an acid form and catalyst inks. 20% C-Pt (E-TEK) and fully-ordered fct-FePt NPs were used as cathode catalysts. Anode catalysts of all the studied cells were 20% C-Pt. The inks were prepared by ultrasonically mixing appropriate amounts of catalyst powders with de-ionized water (Millipore, 18 MΩ cm) and 5% Nafion® suspension (Ion Power, Inc.) for 90 seconds. Subsequently, the inks were brush-painted onto the membrane at 75°C and dried for 30 min. The catalyst loadings were 0.2 $\mathrm{mg_{Pt}/cm^2}$ for all the catalysts tested. The active cell area was 5 $\mathrm{cm^2}$. H_2-air fuel cell testing was carried out in a single cell using a commercial fuel cell test system (Fuel Cell Technologies Inc.). The MEA was sandwiched between two graphite plates with single-serpentine flow channels machined in them. The cell was operated at 80°C. Pure hydrogen and air, humidified at 85°C, were supplied to the anode and cathode at a flow rate of 200 and 500 standard cubic centimeters per minute (sccm), respectively. Both electrodes were maintained at the same absolute pressure of 2.8 bar.

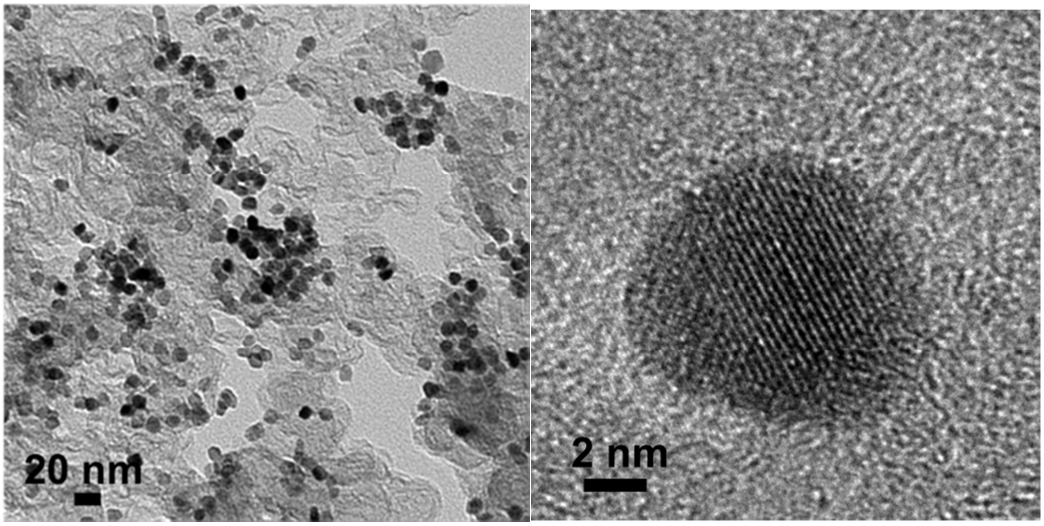

Figure S1. TEM and HRTEM images of the partially ordered fct-FePt deposited on C.

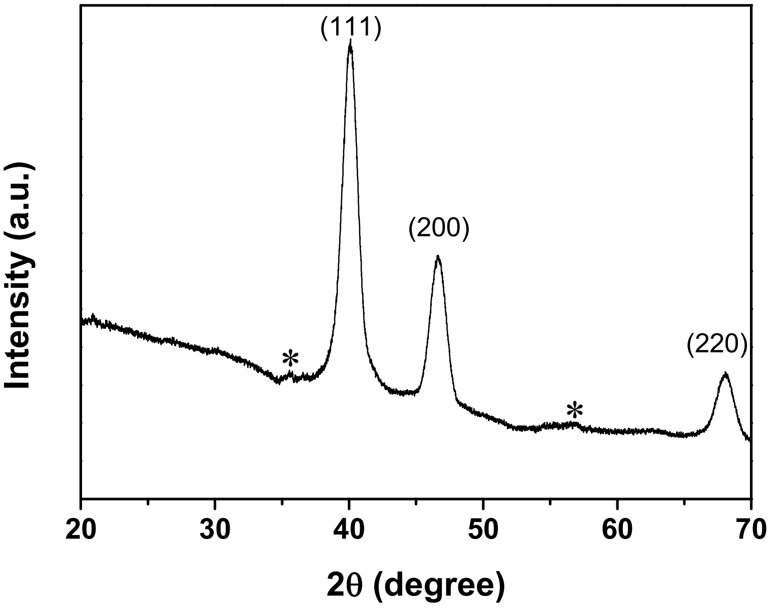

Figure S2. XRD pattern of the as-synthesized dumbbell fcc-FePt-Fe_3O_4 NPs. Due to the small size of Fe_3O_4, the diffraction peaks of Fe_3O_4 are much weaker compared to the strong diffraction peaks of fcc-FePt. * denotes the weak diffraction peaks of Fe_3O_4.

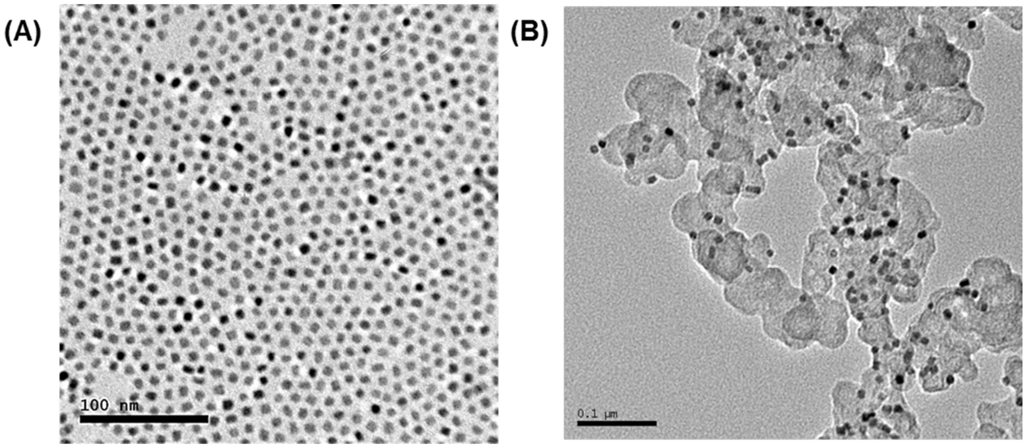

Figure S3. TEM images of 8 nm fcc-FePt NPs and C-fcc-FePt catalyst.

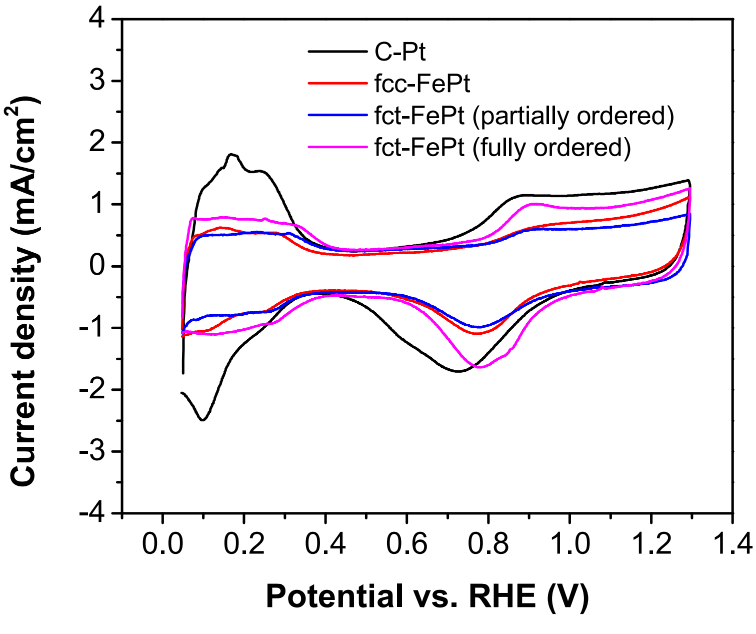

Figure S4. CVs of the commercial Pt, *fcc*-FePt, partially ordered *fct*-FePt and fully ordered *fct*-FePt NPs in N_2-saturated 0.1 M $HClO_4$ with a scan rate of 50 mV/s.

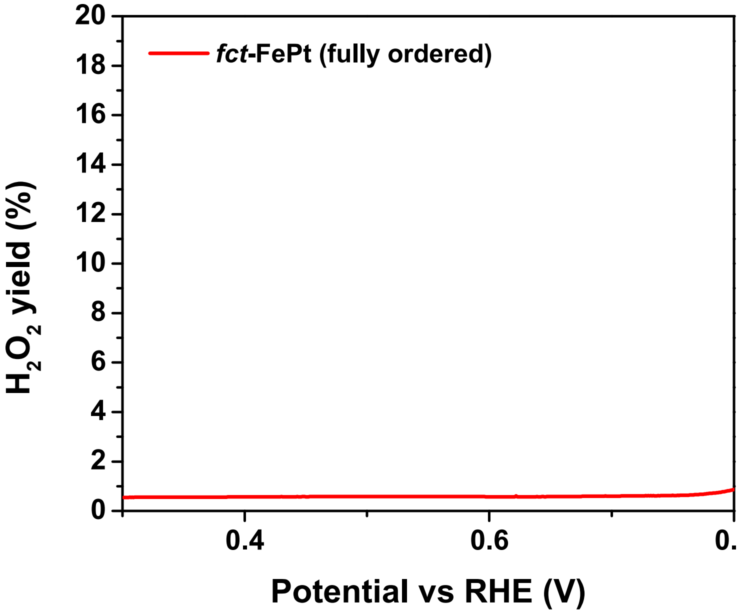

Figure S5. H_2O_2 yield of fully-ordered fct-FePt NPs during ORR in 0.1 M $HClO_4$.

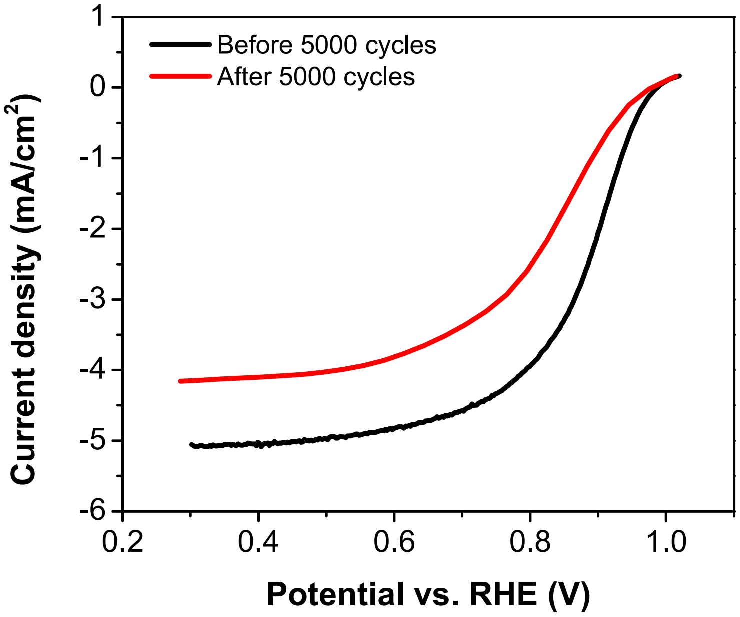

Figure S6. ORR polarization curves of the commercial C-Pt before and after 5000 potential scans between 0.6 and 1.0 V.

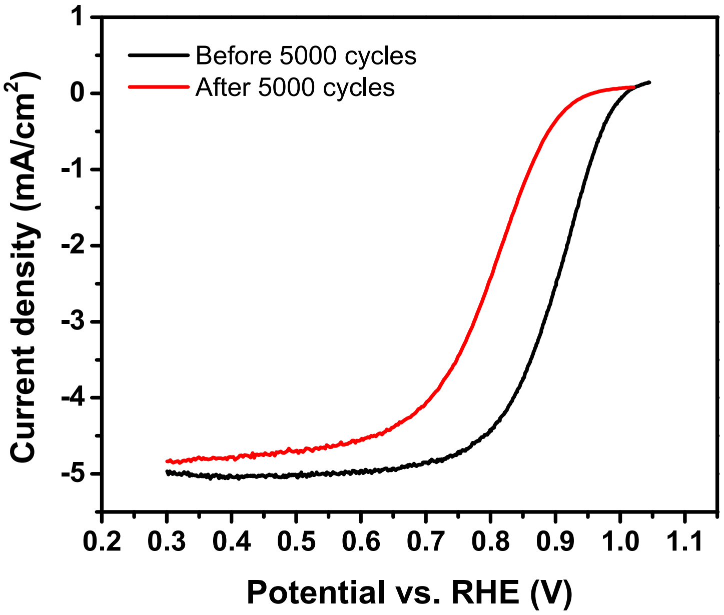

Figure S7. ORR polarization curves of the C-fcc-FePt NPs before and after 5000 potential scans between 0.6 and 1.0 V.

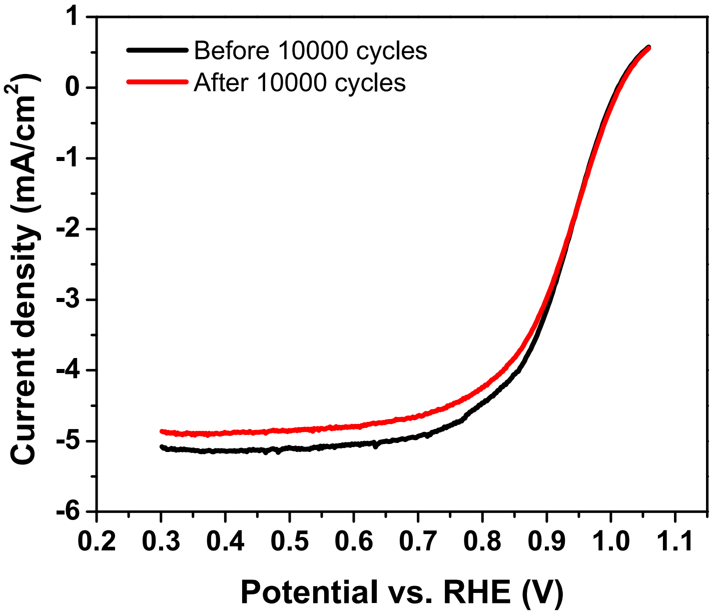

Figure S8. ORR polarization curves of the partially ordered fct-FePt NPs before and after 10000 potential scans between 0.6 and 1.0 V.

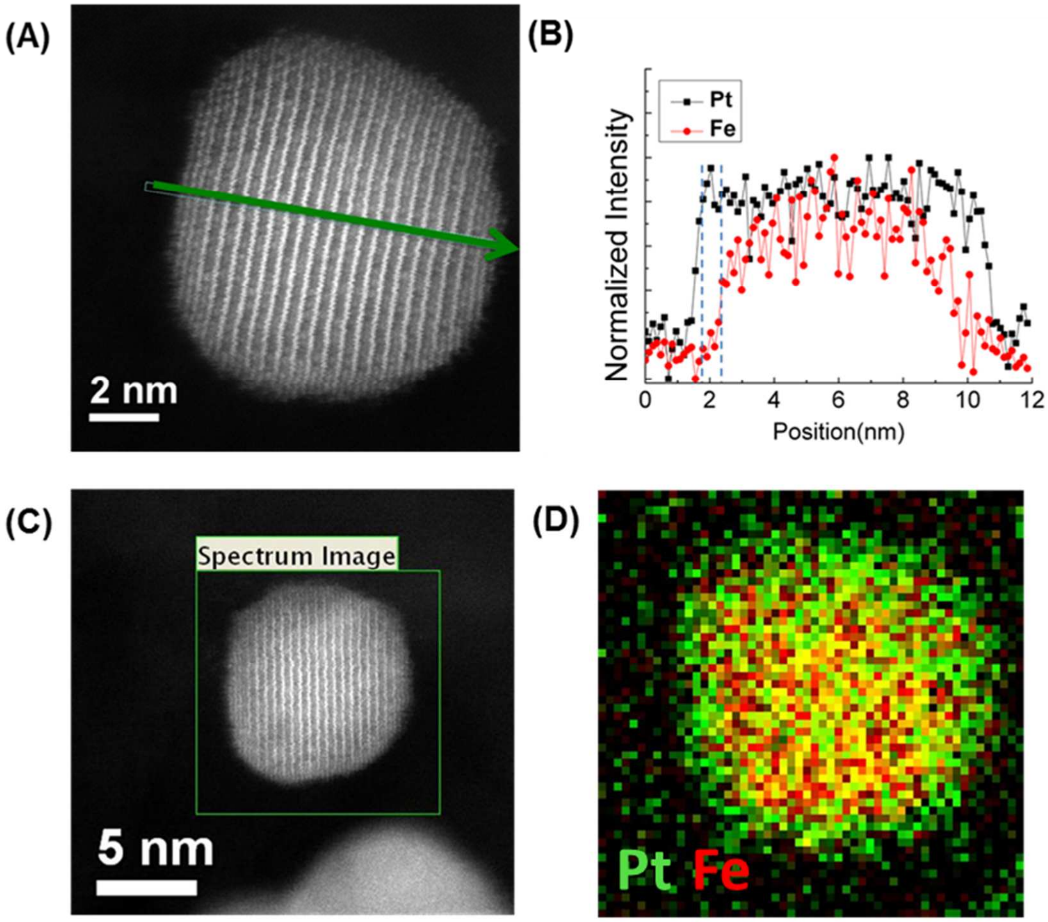

Figure S9. (A) and (C) HAADF-STEM image of a representative fully-ordered fct-FePt NP after 20000 potential cycles. (B) STEM-EELS line scan crossing the fct-FePt NP shown in (A). (D) 2D EELS elemental mapping of the fct-FePt NP shown in (C).

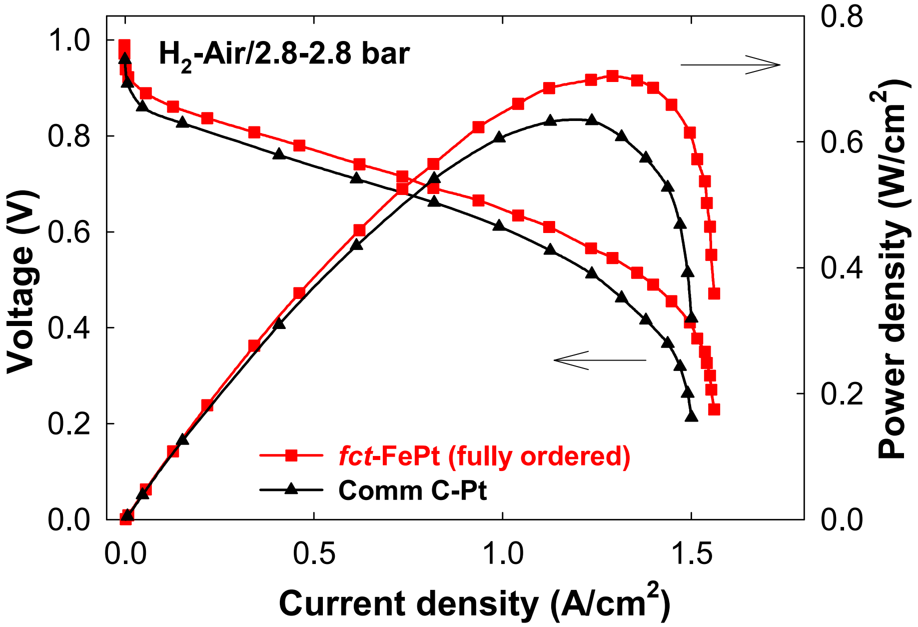

Figure S10. H_2-air fuel cell polarization plots recorded with various cathode catalysts. Anode: 0.2 mg_{Pt}/cm^2 20% C-Pt, 200 scccm H_2, backpressure 2.8 bar; cathode: 0.2 mg_{Pt}/cm^2 20% C-Pt or fully-ordered C-fct-FePt NPs, 500 sccm air, backpressure 2.8 bar; membrane: 2×Nafion® 212; cell temperature: 80ºC.