Electronic Supplementary Material (ESI) for Nanoscale.

Leaching- and Sintering-Resistant Hollow or Structurally Ordered Intermetallic PtFe Alloy Catalyst for Oxygen Reduction Reaction

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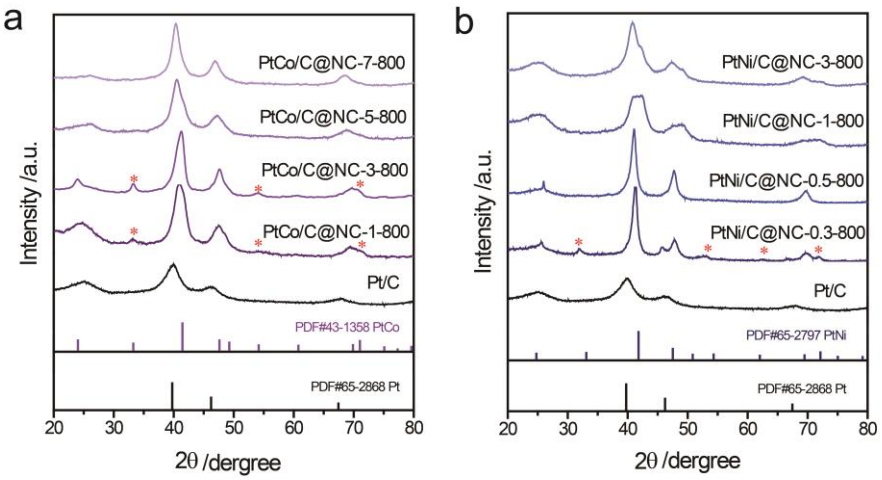

Figure S1 Powder X-ray diffraction patterns of PtCo (a) and PtNi (b) alloy samples obtained at different feeding Co^{2+} or Ni^{2+} contents; the standard powder diffraction data for Pt (PDF card #65-2868), intermetallic PtCo (PDF card #43-1358) and intermetallic PtNi (PDF card #65-2797) are shown for comparison.

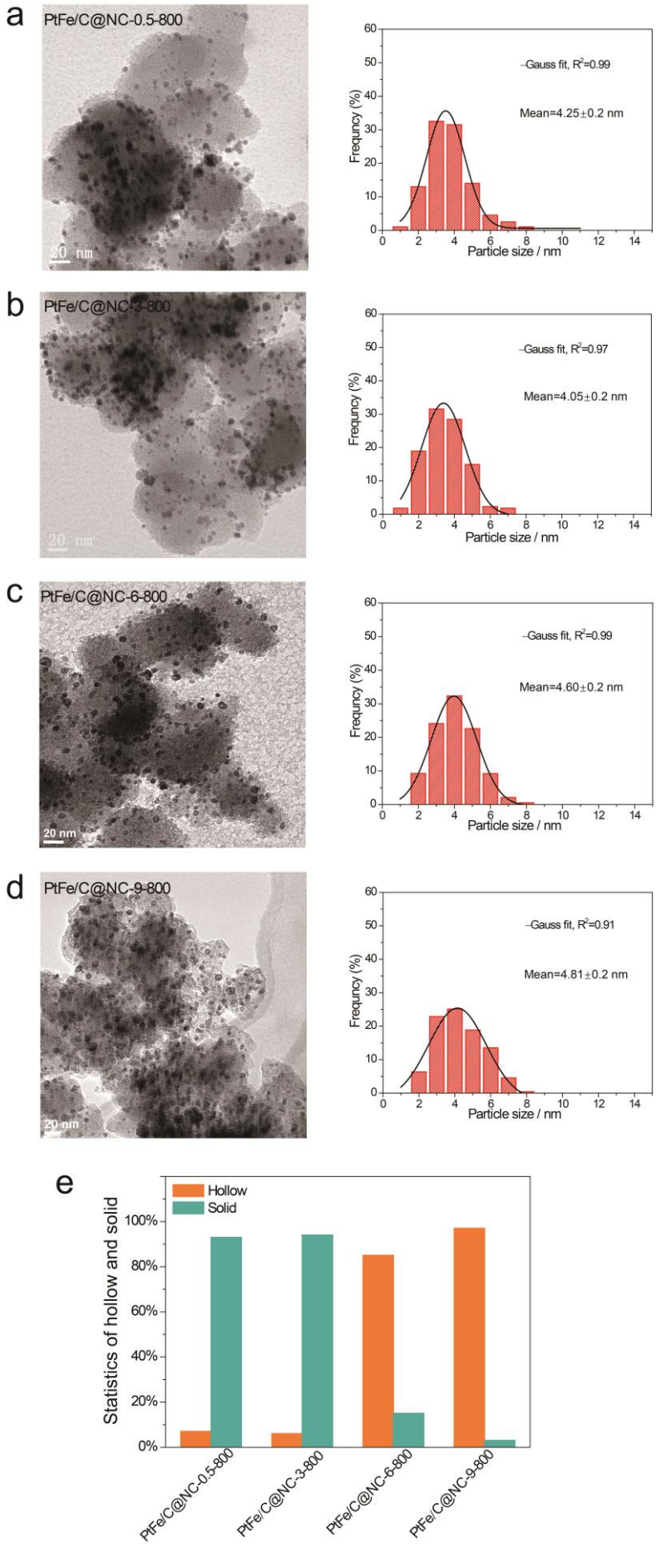
a
PtFe/C@NC-0.5-800
20 nm
Gauss fit, R²=0.99
Mean=4.25±0.2 nm
Frequncy (%)
Particle size / nm
b
PtFe/C@NC-3-800
20 nm
Gauss fit, R²=0.97
Mean=4.05±0.2 nm
Frequncy (%)
Particle size / nm
c
PtFe/C@NC-6-800
20 nm
Gauss fit, R²=0.99
Mean=4.60±0.2 nm
Frequncy (%)
Particle size / nm
d
PtFe/C@NC-9-800
20 nm
Gauss fit, R²=0.91
Mean=4.81±0.2 nm
Frequncy (%)
Particle size / nm
e
Hollow
Solid
Statistics of hollow and solid
PtFe/C@NC-0.5-800
PtFe/C@NC-3-800
PtFe/C@NC-6-800
PtFe/C@NC-9-800

Figure S2 TEM images, particle distribution histograms and particle morphology statistics (**e**) of PtFe/C@NC-0.5-800 (**a**), PtFe/C@NC-3-800 (**b**), PtFe/C@NC-6-800 (**c**) and PtFe/C@NC-9-800 (**d**).

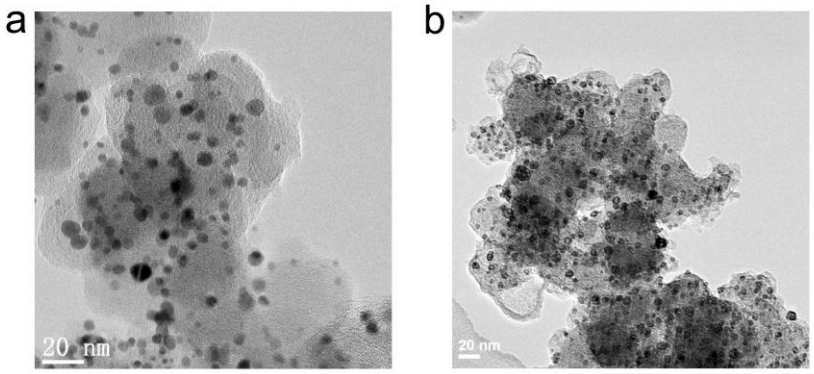

Figure S3 TEM images of PtFe/C@NC-9-800 samples after treatment with NaOH (**a**) or HF (**b**).

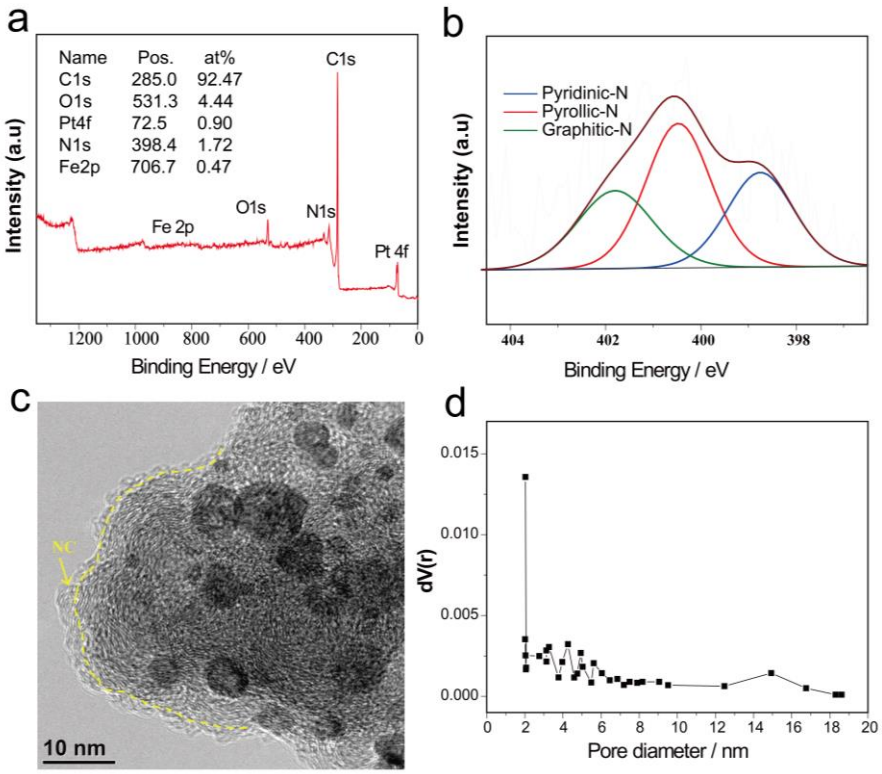

Figure S4 XPS survey (**a**), N1s XPS spectra (**b**), HRTEM image (**c**) and pore size distribution from the BJH method of PtFe/C@NC-9-800 catalyst.

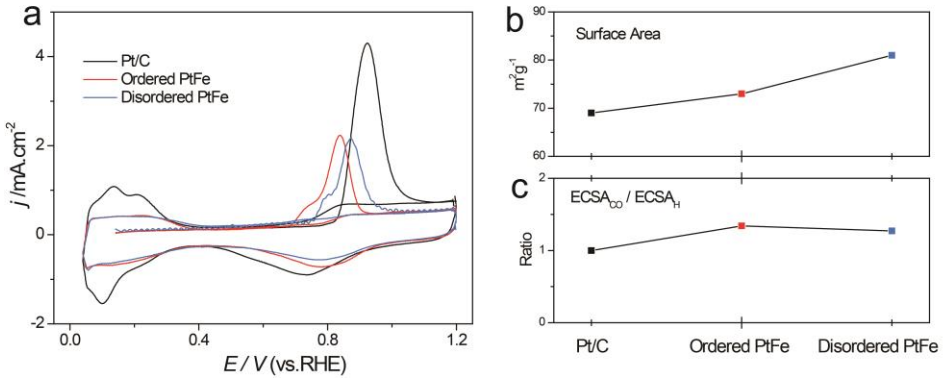

Figure S5 (a) The CO stripping curves of ordered PtFe (PtFe/C@NC-3-800), disordered PtFe (PtFe/C@NC-9-800) and Pt/C catalysts recorded at room temperature in CO-saturated 0.1 M $HClO_4$ solution. (b) The specific electrochemically active surface area values of ordered PtFe (PtFe/C@NC-3-800), disordered PtFe (PtFe/C@NC-9-800) and Pt/C catalysts calculated from the ECSA-CO and Pt mass loaded on the RDE working electrode. (c) The ratio between ECSA values determined by ECSA-CO and ECSA-H_{upd}.

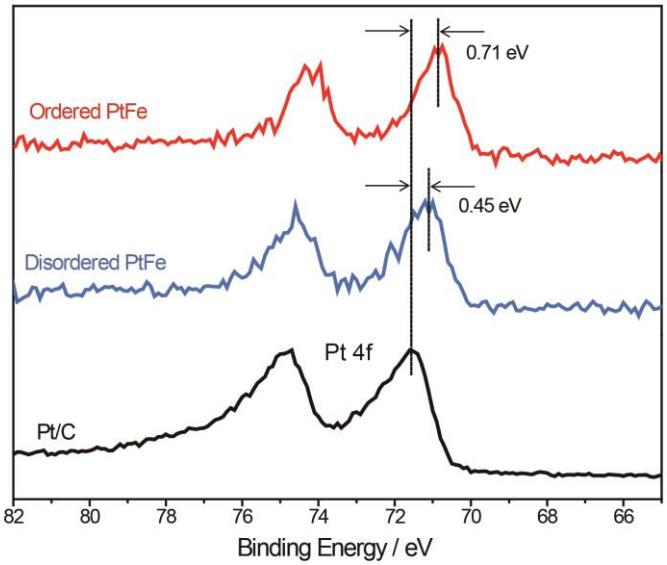

Figure S6 Pt 4f XPS spectra of ordered PtFe (PtFe/C@NC-3-800), disordered PtFe (PtFe/C@NC-9-800) and Pt/C catalysts.

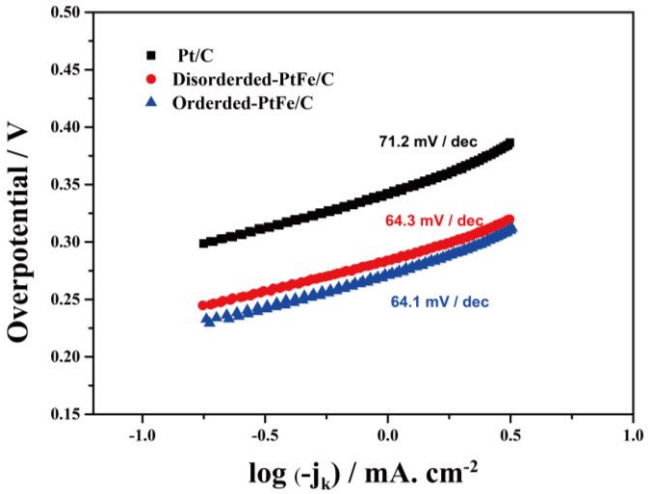

Figure S7 The Tafel curves of ordered PtFe (PtFe/C@NC-3-800), disordered PtFe (PtFe/C@NC-9-800) and Pt/C catalysts.

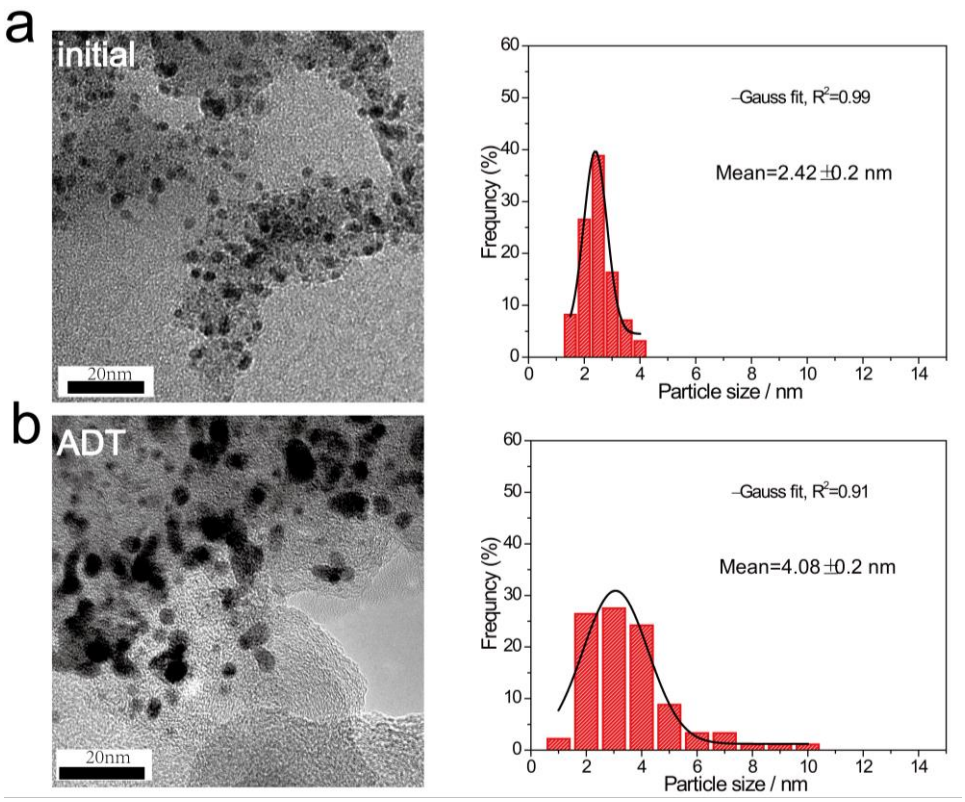

Figure S8 TEM images and particle-distribution histograms of a commercial Pt/C catalyst before (**a**) and after (**b**) 30,000 CV cycles between 0.6 and 1.1 V in O_2-saturated 0.1 M $HClO_4$ at a scan rate of 50 mV s^{-1}.

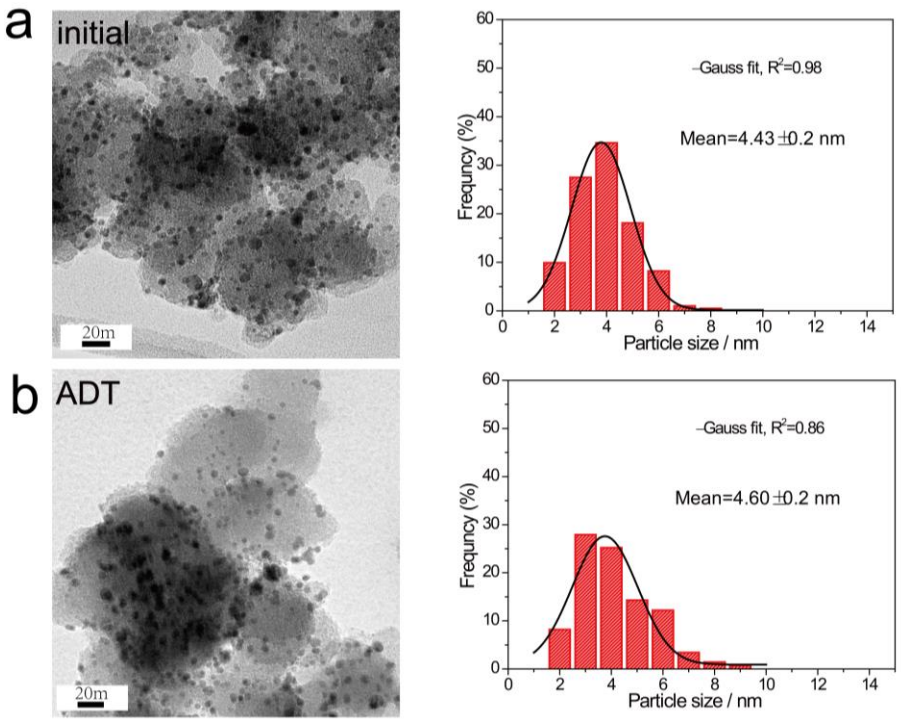

Figure S9 TEM images and particle-distribution histograms of ordered PtFe (PtFe/C@NC-3-800) catalyst before (**a**) and after (**b**) 30,000 CV cycles between 0.6 and 1.1 V in O_2-saturated 0.1 M $HClO_4$ at a scan rate of 50 mV s^{-1}.

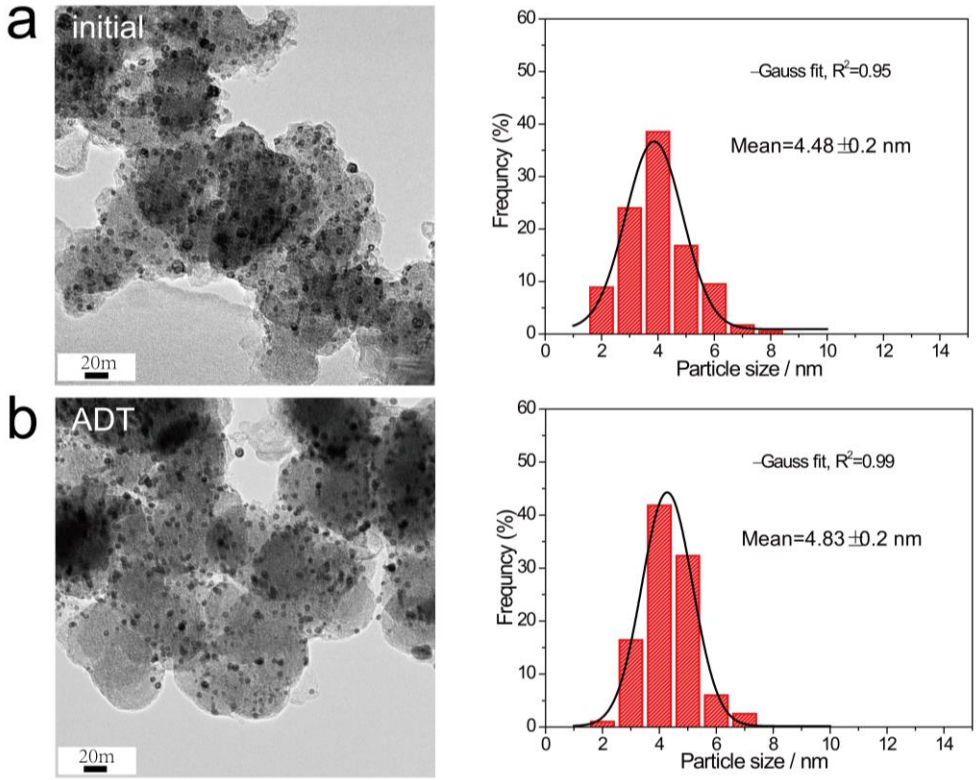

Figure S10 TEM images and particle-distribution histograms of disordered PtFe (PtFe/C@NC-9-800) catalyst before (**a**) and after (**b**) 30,000 CV cycles between 0.6 and 1.1 V in O_2-saturated 0.1 M $HClO_4$ at a scan rate of 50 mV s^{-1}.

Sample	2θ/degree (111)	Lattice parameter (1/Å)	Lattice constant (%)
Pt/C JCPDS:65-2868	39.761	0.2206	----
Ordered PtFe alloy	40.433	0.2261	2.50
Disordered PtFe alloy	40.315	0.2238	1.45

Table S1. The parameters of catalysts According to the XRD patterns and the Debye-Scherrer equation.

Sample	Pt loading (ug)	ECSA-CO (m^2/g)	Half-wave potential (V)	Exchange currents density (A/cm^2)	Mass activity @0.9V (A/mgPt)	Specific activity @0.9V (mA/cm^2)
Pt/C	5.90	69	0.905	7.1×10^{-6}	0.22	0.31
Ordered PtFe alloy	3.18	73	0.933	7.6×10^{-5}	1.48	2.03
Disordered PtFe alloy	2.82	81	0.930	7.4×10^{-5}	1.47	1.81

Table S2. Pt loading from ICP-MS, ECSA-CO, half-wave potential, the exchange currents and the calculated mass activity and specific activity at 0.9V of commercial Pt/C, ordered PtFe alloy (PtFe/C@NC-3-800) and disordered PtFe alloy (PtFe/C@NC-9-800) catalysts.

Sample	Initial				After 30k CV cycles			
	half-wave potential (V)	mass activity @0.9V (A/mg Pt)	specific activity @0.9V (mA/cm^2)	Pt/Fe molar ratio	Half-wave potential (V)	mass activity @0.9V (A/mg Pt)	specific activity @0.9V (mA/cm^2)	Pt/Fe molar ratio
Pt/C	0.905	0.22	0.31	No	0.864	0.082	0.185	No
Ordered PtFe alloy	0.933	1.48	2.03	76.9/23.1	0.927	1.17	1.65	78.2/21.8
Disordered PtFe alloy	0.930	1.47	1.81	87.7/12.3	0.919	0.85	1.18	91.7/8.3

Table S3. Half-wave potential, the calculated mass activity and specific activity at 0.9V, and the Pt/Fe molar ratio from ICP-MS before and after 30K CV cycles of commercial Pt/C, ordered PtFe alloy (PtFe/C@NC-3-800) and disordered PtFe alloy (PtFe/C@NC-9-800) catalysts.