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Synthesis of hierarchical Pd$_4$Fe nanoflowers and their electrocatalytic performance for oxygen reduction reaction

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Experimental details

1. Reagents and characterization

Palladium acetylacetonate, Pd/C (20 wt%) and Pt/C (20 wt%) were obtained from Alfa Aesar. Oleylamine was purchased from J&K Scientific. Vulcan XC-72 powder was obtained from Cobot Co. (USA). Nafion® solution in low aliphatic alcohols and water (5 wt.%) was supplied by Aldrich. The water used in all experiments was ultra-pure water (18.2 MΩ·cm at 25 °C). Other reagents were of analytical grade and used without further purification.

Transmission electron microscopy (TEM) images were taken on a JEOL JEM-1200EX transmission electron microscope operating at 100 kV. High-resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) characterization were performed by a FEI Tecnai G^{2}F20 S-Twin high-resolution transmission electron microscope operating at 200 kV. Scanning electron microscopy (SEM) image was recorded by a LEO-1530 field emission scanning electron microscope. The powder X-ray diffraction (XRD) patterns

were recorded with a Bruker D8-advance X-ray powder diffractometer with Cu Kα (λ= 1.5406 Å) at an accelerating potential of 40 kV and a tube current of 40 mA. X-ray Photoelectron Spectroscopy (XPS) measurement was carried out with an Axis Ultra photoelectron spectrometer using an AlKα (1486.7 eV) X-ray source, with the pressure of the measuring chamber set at 5×10^{-9} Torr. The binding energy scales for the samples were referenced by setting the C 1s binding energy of contamination carbon to 284.8 eV. The composition of the hierarchical Pd_4Fe nanoflowers (Pd_4Fe NFs) was analyzed by the inductively coupled plasma atomic emission spectrometer (ICP-AES), energy dispersive spectrometer (EDS) and XPS.

2. Preparation of Pd_4Fe NFs

In a typical experiment, a mixture of palladium acetylacetonate (50 mg) and oleylamine (10 mL) was stirred at 120 °C under argon atmosphere. After the palladium acetylacetonate was dissolved in the oleylamine, 50 μL of $Fe(CO)_5$ was quickly injected into the hot solution. The reaction was kept at 120 °C under argon atmosphere for an hour without stirring. The black solution was then cooled to room temperature and centrifuged in excess ethanol. The precipitate was redispersed in cyclohexane and washed by ethanol for three times. The final product was dispersed in 10 mL of cyclohexane for further use.

For control experiments, all the procedures were the same as that for preparing Pd_4Fe NFs except altering only one reaction condition. For example, preparation in the absence of $Fe(CO)_5$, reduction with 5 mL of $Fe(CO)_5$ but no oleylamine or reduction in oleylamine by bubbling CO gas instead of $Fe(CO)_5$.

3. Electrochemical measurements

The electrocatalytic properties of Pd_4Fe NFs were investigated in an aqueous solution of $HClO_4$ (0.1 M) or KOH (0.1 M).

Electrochemical measurements were performed in a conventional three-electrode cell with a rotating disk electrode (RDE) (Pine Research Instrumentation Inc., USA) connected to a CHI 660C potentiostat (Chenhua Instrument Co., China). Pt foil and standard hydrogen electrode were used as counter and reference electrode, respectively. The working electrode was a glassy carbon rotating disk electrode (5

mm diameter, 0.196 cm^2 geometrical surface area). All potentials in this work were referred to the reversible hydrogen electrode (RHE).

4 Preparation of working electrodes

In order to avoid being unduly covered by redundant Nafion®, Pd$_4$Fe NFs were supported on carbon support before the preparation of working electrodes. In a typical experiment, 80 mg of Vulcan XC-72 carbon was added into 200 mL of ethanol, and ultrasonically dispersed for 30 min. A certain amount of the product containing 20 mg of Pd$_4$Fe NFs was added to the above mixture dropwise. Then the mixture was stirred for three days at room temperature. After being filtered and washed by ethanol, the catalysts were dried in a vacuum oven overnight at 40 °C.

To prepare the working electrode, 5.0 mg of Pd$_4$Fe NFs catalysts (18 wt%) were dispersed in 8.0 mL of water-isopropanol solution with a volume ratio of 3:1. The dispersion was sonicated for 15 minutes to form a homogeneous ink. Then, 10 μL of Nafion® solution was added and ultrasonicated for another 15 minutes. 10 μL of the as-obtained suspension was transferred onto a freshly polished glassy carbon RDE and dried at room temperature. The loading of Pd was ca. 6 μg·cm^{-2} on the electrode.

For comparison, working electrodes for the commercial Pd/C (20 wt%) and Pt/C (20 wt%) catalysts were also prepared with the aforementioned procedure. The loading of Pd or Pt was ca. 6 μg·cm^{-2} on the electrode likewise.

5 Electrochemical surface area

Prior to use, the as-prepared electrodes were continuously cycled at a sweep rate of 500 mV·s^{-1} for at least 50 cycles in N$_2$-saturated electrolyte solution at 30 °C, until stable cyclic voltammograms (CVs) were obtained. The electrochemical surface areas (ECSAs) of the tested catalysts were calculated from CVs by integrating the area of the hydrogen under-potential deposition (H$_{UPD}$) region (210 μC·cm^{-2}) after double-layer correction in the acidic electrolyte, or integrating the reduction region of platinum/palladium oxide formed on the top layer (420 μC·cm^{-2}) after double-layer correction in the alkaline electrolyte.

6 Oxygen reduction reaction

Oxygen reduction reaction (ORR) activities were measured at 1600 rpm with

scan rates of 10 and 20 mV·s^{-1} in O$_2$-saturated electrolyte solution at 30 °C. The electrochemical catalytic activities of the catalysts in the presence of methanol (0.1 M) were evaluated at 1600 rpm with a scan rate of 20 mV·s^{-1}. ORR polarization curves were obtained from the difference of current densities between O$_2$ and N$_2$ atmosphere ($i_{O_2-N_2} = i_{O_2} - i_{N_2}$). The kinetic current density (i_k) was calculated based on the Koutecky-Levich equation:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} \quad (1)$$

where i is the measured current and i_d is the diffusion-limiting current. For all catalysts, i_k calculated from Eq. (1) was normalized by Pd or Pt loading on the electrodes and ECSA in order to obtain mass and specific activity, respectively.

7 Accelerated aging tests

Accelerated aging tests (AATs) were carried out by cycling the potential between 0.6 and 1.0 V for 5000 cycles at 400 rpm with a scan rate of 100 mV·s^{-1} in O$_2$-saturated KOH solution (0.1 M) at 30 °C.
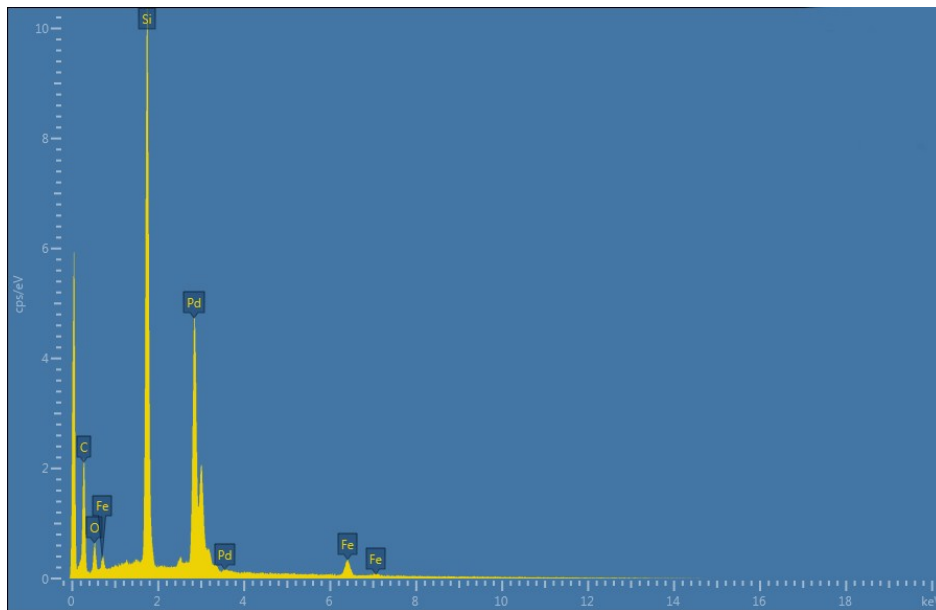

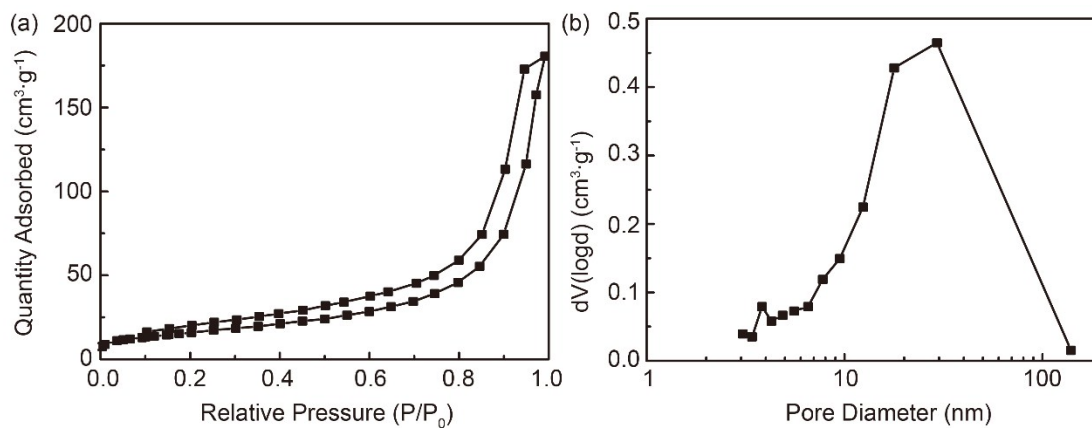**Fig. S1** EDS spectrum of the Pd$_4$Fe NFs.

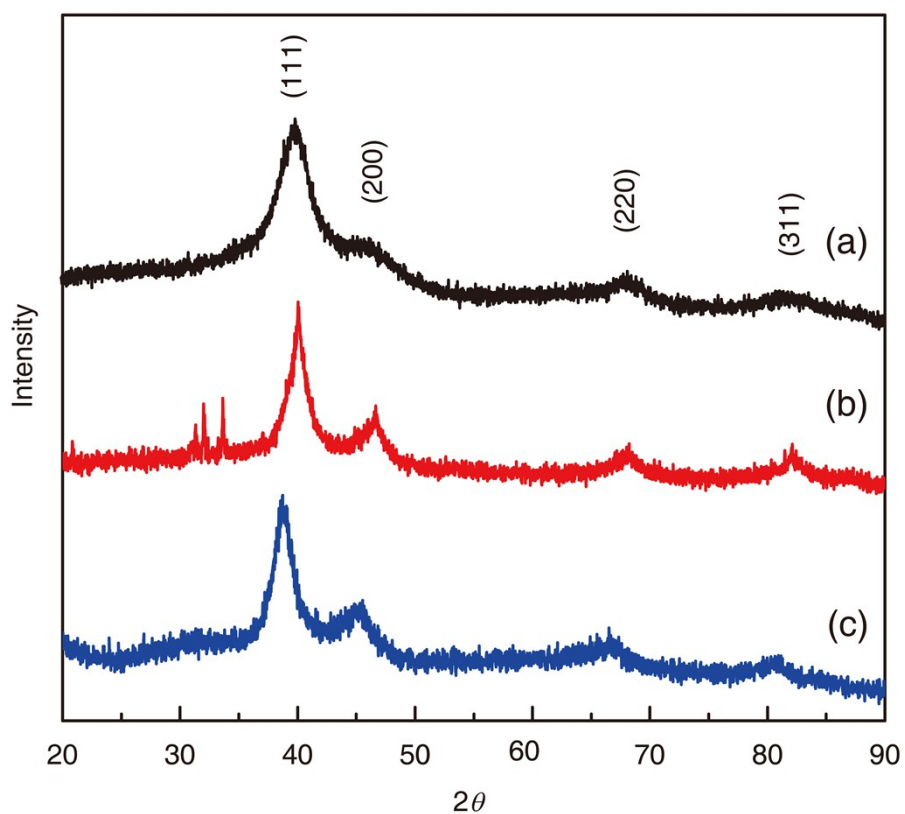**Fig. S2** Adsorption isotherms (a) and pore size distribution (b) of the prepared Pd$_4$Fe NFs.

Fig. S3 XRD patterns of the prepared Pd$_4$Fe NFs (a) and the products of the control experiments that reduced palladium acetylacetonate with only 5 mL of Fe(CO)$_5$ (b) and only oleylamine (c).
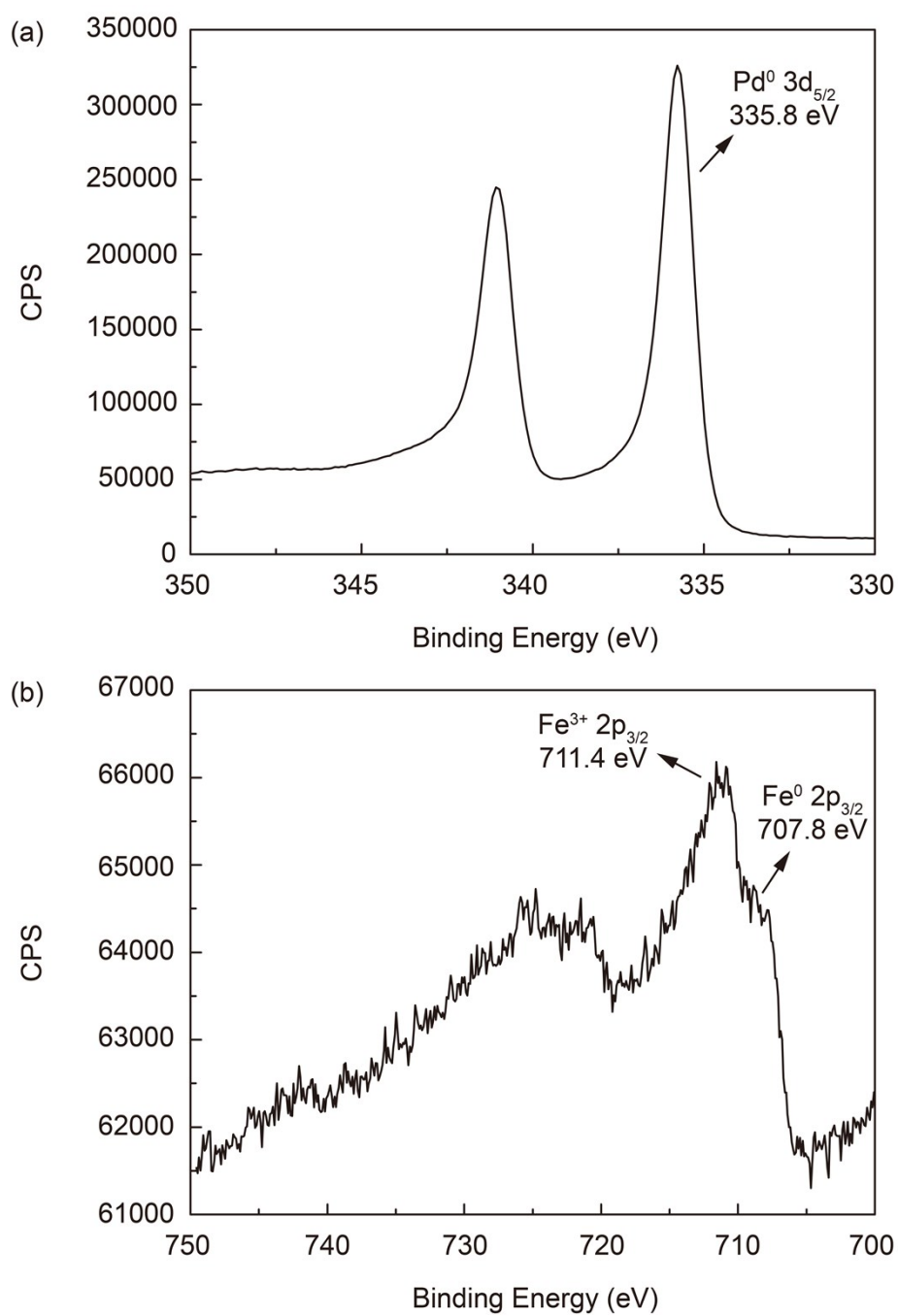
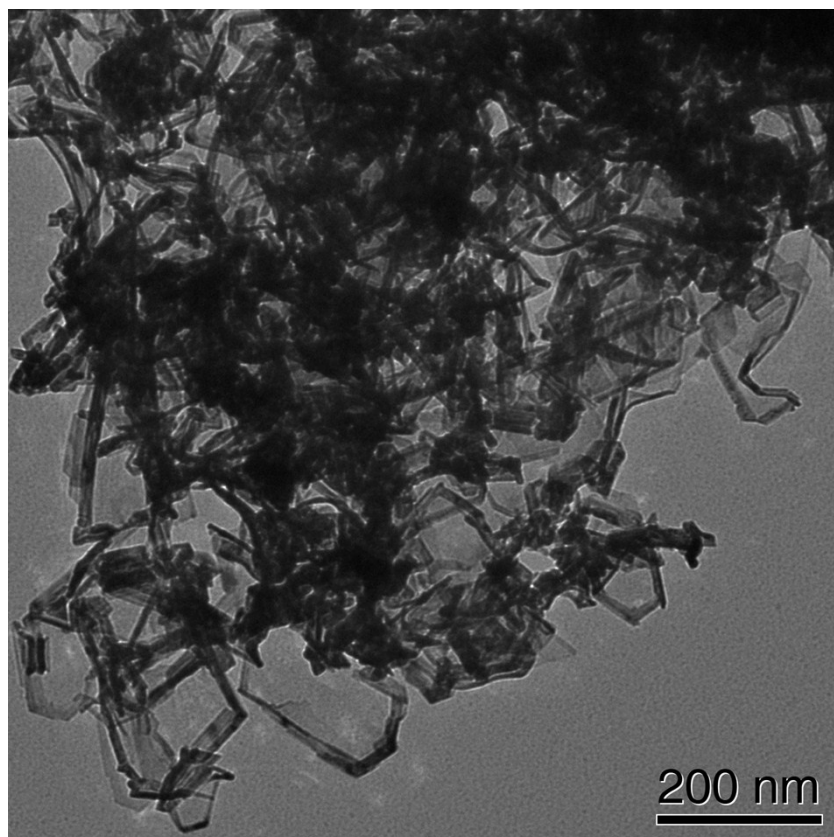**Fig. S4** XPS spectra of the Pd 3d (a) and Fe 2p (b) of the prepared Pd$_4$Fe NFs.

Fig. S5 TEM image of the products of the control experiments by inducing CO instead of Fe(CO)$_5$.
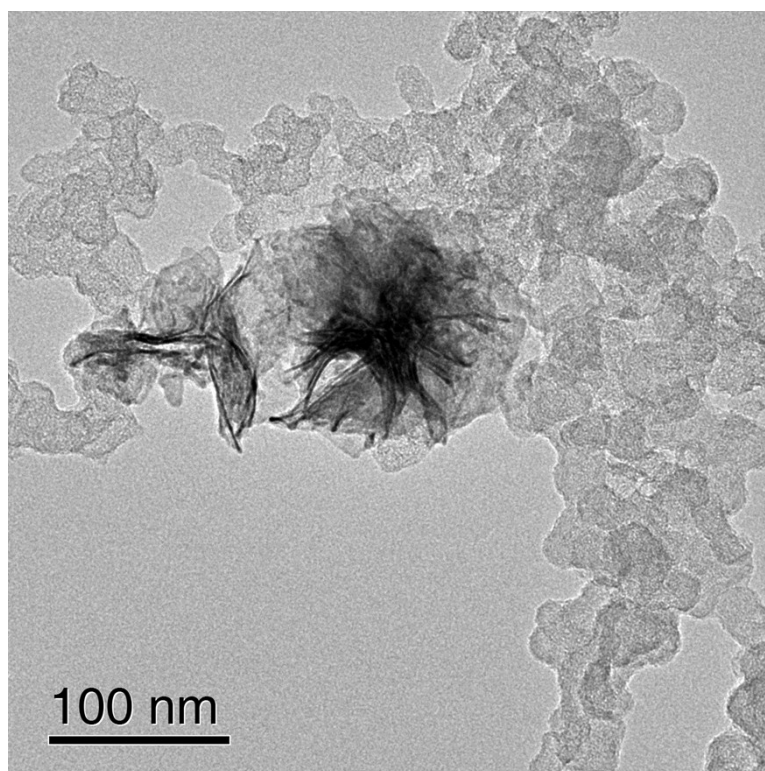

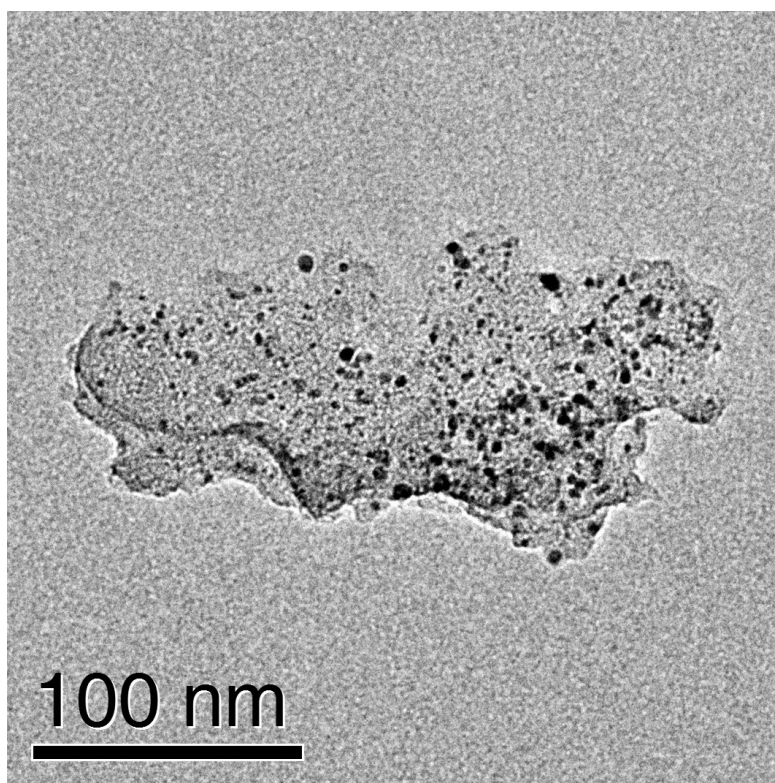**Fig. S6** TEM image of carbon supported Pd$_4$Fe NFs.

Fig. S7 TEM image of the commercial Pd/C catalyst.
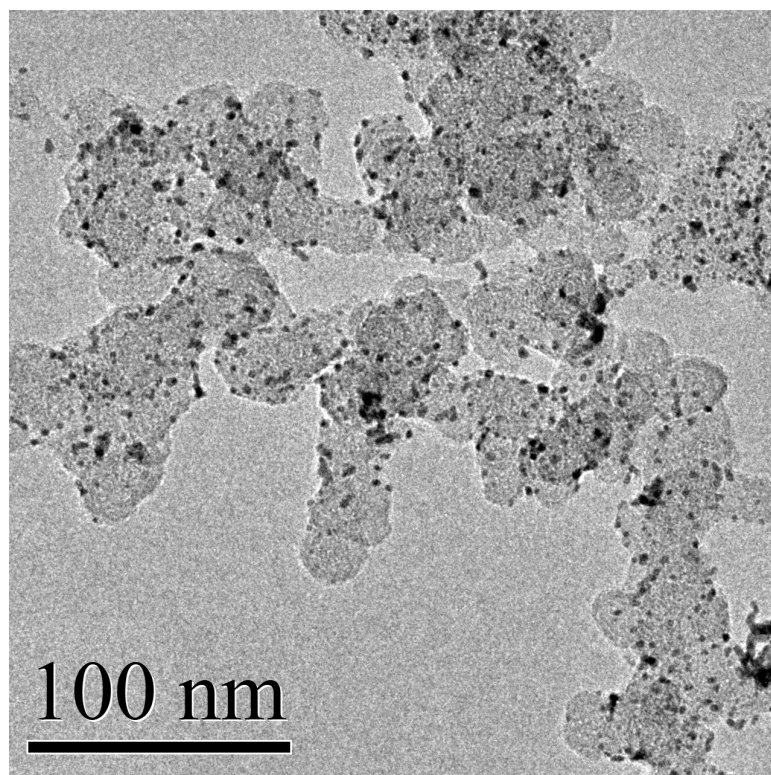

Fig. S8 TEM image of the commercial Pt/C catalyst.
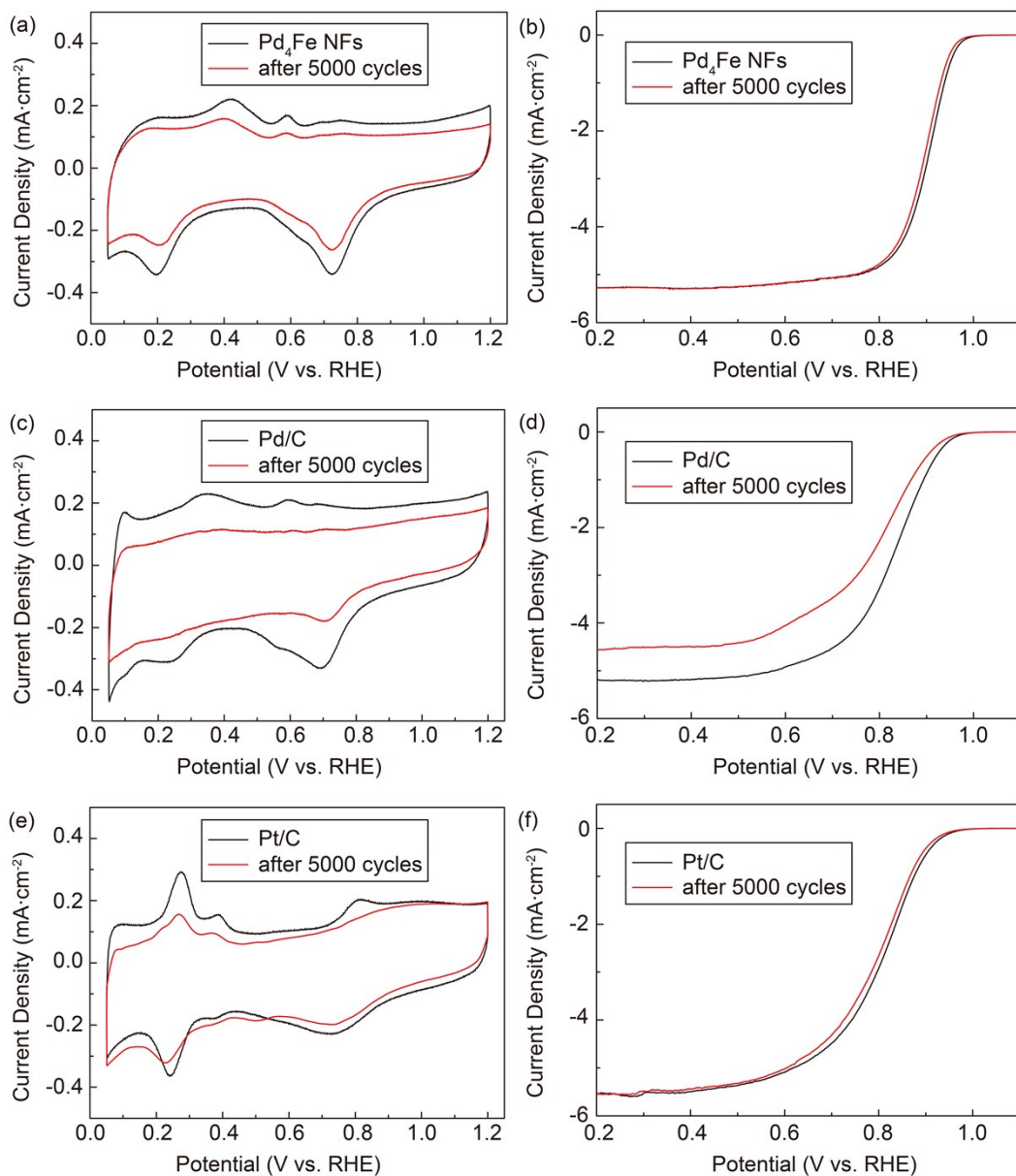
Fig. S9 Electrochemical properties of Pd$_4$Fe NFs, Pd/C, and Pt/C catalysts before and after AATs: CVs at a scan rate of 50 mV·s^{-1} under N$_2$ flow (a, c and e); ORR polarization curves at a scan rate of 20 mV·s^{-1} under O$_2$ flow and a rotation rate of 1600 rpm (b, d and f).

Fig. S10 ORR polarization curves of Pd$_4$Fe NFs, Pd/C, and Pt/C catalysts in the acidic electrolyte (a) and in the alkaline electrolyte (b) with and without methanol (0.1 M).

Table S1 The measured mole ratio of Pd to Fe in the prepared Pd_4Fe NFs.
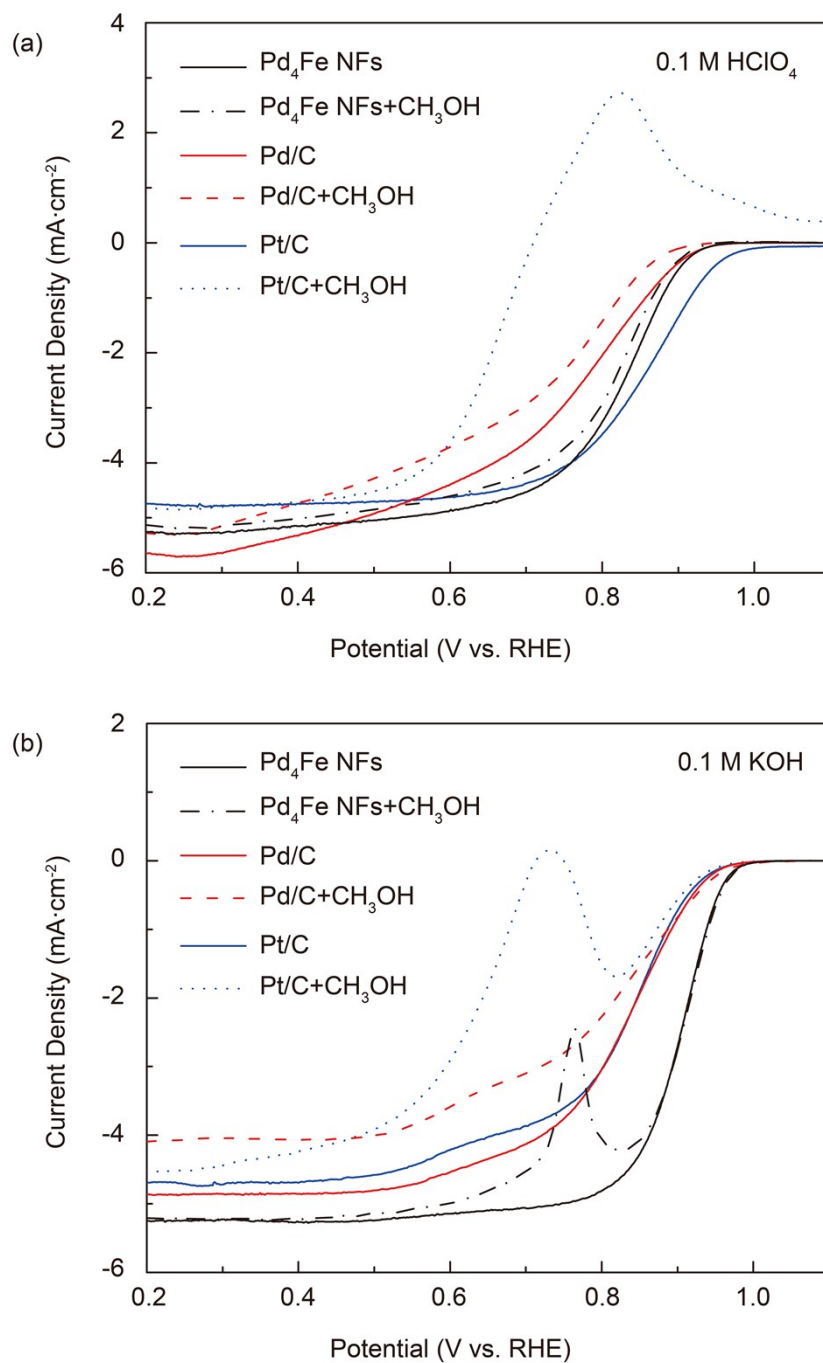
Analysis technique	Pd:Fe
ICP-AES	80.4:19.6
EDS	80.8:19.2
XPS	83.9:16.1

Table S2 Comparison of ORR electrocatalytic activities of different Pd based catalysts in the acidic electrolytes.[a]

Catalyst	Half-wave potential (V)	Specific activity (mA·cm^{-2}$_{Pd}$)		Mass activity (mA·mg^{-1}$_{Pd}$)		Scan rate (mV·s^{-1})	Reference
		0.85 V	0.9 V	0.85 V	0.9 V		
Pd$_4$Fe NFs	0.833	1.57	0.26	521	86	20	This work
Pd$_4$Fe NFs	0.821	1.06	0.16	353	55	10	This work
Pd/C	0.778	0.47	0.13	228	62	20	This work
Pd/C	0.772	0.36	0.09	178	44	10	This work
Pd$_3$Fe/C	0.832	0.12		121		20	[1]
HT Pd$_3$Fe	0.82		0.045		15	5	[2]
O-Pd$_3$Fe/C	0.767	0.12[b]		104[b]		5	[3]
Pd$_3$Co (OHT)	0.86	0.45	0.12	452		20	[4]
Ni@Pd3/C NPs	0.87		0.08	105	25	5	[5]

[a] All potentials given were referred to the reversible hydrogen potential (RHE). [b] This value was calculated at 0.8 V.

Table S3 Comparison of ORR electrocatalytic activities of different Pd/Pt based catalysts in the alkaline electrolytes.[a]

Catalyst	Half-wave potential (V)	Specific activity[b] (mA·cm$^{-2}_{PGM}$)		Mass activity[b] (mA·mg$^{-1}_{PGM}$)		Scan rate (mV·s^{-1})	Reference
		0.85 V	0.9 V	0.85 V	0.9 V		
Pd$_4$Fe NFs	0.903	11.60	2.78	4069	975	20	This work
Pd/C	0.832	1.83	0.57	510	160	20	This work
Pt/C	0.835	2.44	0.64	514	135	20	This work
PdCuNi-AB-t/C	0.90				450	10	[6]
Pt$_{13}$Pd$_{87}$NT			1.48		333	10	[7]
ordered Pd$_3$Fe/C				220[c]	97	10	[8]
AuPdCo/C Intermetallic					130[d]	10	[9]
ordered Pd$_3$Pb/C	0.92				169	10	[10]
ordered PdCuCo NPs/C	0.872			380[c]	130	10	[11]

[a] All potentials given were referred to the reversible hydrogen potential (RHE). [b] The value was normalized in reference to the loading amount of all platinum group metal (PGM, include Pt and Pd). [c] The value was estimated based on the histograms at 0.875 V. [d] This value was quantified by calculating the precious metal mass.

Reference:

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