Supplementary information

Ordered intermetallic PtFe@Pt core-shell nanoparticles supported on the carbon nanotubes with superior activity and durability as oxygen reduction reaction electrocatalysts

Haijing Liu, Meiling Dou, Feng Wang,* Jingjun Liu, Jing Ji and Zhilin Li

State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, P R China

Experimental

Sample preparation. The ordered intermetallic PtFe@Pt/CNT electrocatalyst was synthesized by a modified NaBH-reduction method followed by heat-treatment under Ar atmosphere. Multi-walled carbon nanotubes (CNTs) as the support material were firstly refluxed in mixed solution of high concentrated H_2SO_4 and HNO_3 (volume ratio of 3:1) at 70 °C for 6 hours. The resulting product was filtered and rinsed with deionzed water for several times. In a typical synthesis of CNTs supported PtFe alloy nanoparticles, 50 mg of CNTs was dispersed in 100 mL ethylene glycol containing 33.0 mg of H_2PtCl_6• $6H_2O$ with sonication for 30 min. Another 50 mL ethylene glycol dissolved with 11.5 mg of $Fe(NO_3)_2$ were gradually added to the above suspension and stirred for 30 min. The mixture was heated to 80 °C under continuously stirring, and then excessive NaBH aqueous (0.1 mol/L) solution was added in droplets. After being kept at 80 °C for another 3 hours, the resulting sample was collected by filtering

and rinsed by ethanol for several times, followed by drying at 80 °C in vacuum oven for 24 hours. The as-prepared CNTs supported PtFe alloy nanoparticles were annealed at 350 °C and 650 °C for 2 hours, and finally cooled to room temperature under Ar atmosphere. Commercial Pt/C electrocatalysts (Hispec3000, Johnson Matthey, loading rate: 20 wt.%) was applied as one of the reference samples.

Characterization. The TEM was conducted using JEOL JSM-2100 microscopy with an acceleration voltage of 200 kV. The HAADF-SEM images and EDX elemental analysis were taken on a JEOL JEM-ARM200F microscopy. Powder XRD measurement was carried out on Rigaku D/max-2500 with a Cu Kα (α=1.54 Å). Determination of the elements amount was performed by means of ICP-MS (ICPS-7500, Shimadzu).

Electrochemical measurements. Electrochemical measurements were carried out using a conventional three-electrode cell at room temperature with an AUTOLAB PGSTAT302N electrochemical workstation. Pt foil was served as the counter electrode, and a saturated calomel electrode (SCE) was used as reference electrode. The working electrode was prepared by mixing 5 mg electrocatalysts with 50 μL nafion solution (5 wt %, DuPont USA) in 1 mL ethanol by sonication. A measured value (10 μL) of the mixture was casted onto a glassy carbon rotating disk electrode (0.1256 cm^2 geometrical area), and the solvent was evaporated under vacuum. The Pt loading on the electrode is 0.01 mg/cm^2, and all the potentials are referred to reversible hydrogen electrode (RHE). Cyclic voltammetry was carried out at potential range of 0.02 V to 1.02 V in 0.1 mol/L $HClO_4$ solution saturated with N_2 at a scan rate

of 50 mV/s. The electrochemical surface area (ECSA) was calculated according to the hydrogen desorption charge between 0.02 V to 0.4 V with the equation:

$$ECSA = Q_H / ([Pt] \times 0.21)$$

where [Pt] represents the Pt loading (mg/cm^2) on the electrode, Q_H is the charge for H_{upd} adsorption/desorption (mC/cm^2), and 0.21mC represents the charge required to oxidize a monolayer of hydrogen. The polarization curves were recorded in 0.1 mol/L $HClO_4$ solution saturated with O_2 at a scan rate of 5 mV/s under rotating rate of 1225 rpm. The kinetic current was calculated applying the Koutecky-Levich equation:

$$1/i = 1/i_k + 1/(0.62nFCo_2Do_2^{2/3}\nu^{-1/6}\omega^{1/2})$$

where i_k is the kinetic current density, i is the measured current density, n is the number of electrons for the ORR process, F is the Faraday constant, Do_2 is the diffusion coefficient, ν is the kinematic viscosity, Co_2 is the bulk concentration of O_2, ω is the rotation rate.

Figures & Tables

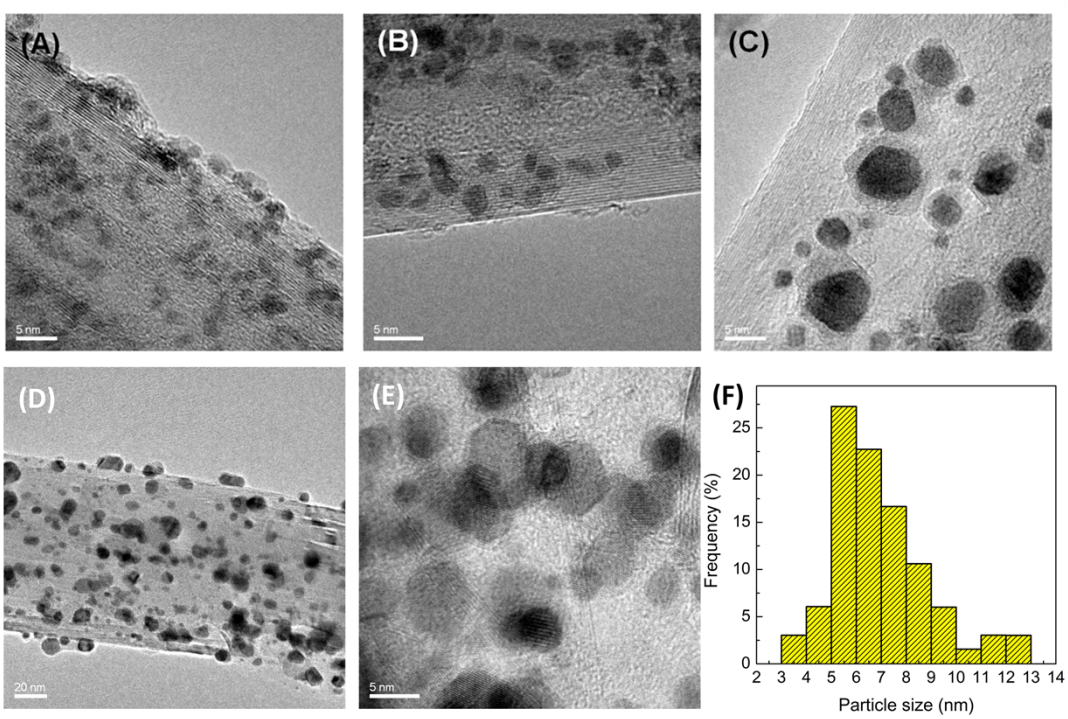

Fig. S1 TEM images of (A) PtFe/CNT, (B) PtFe/CNT annealed 350 °C, (C) (D) (E) PtFe/CNT annealed at 650 °C and the corresponding particle size distribution graph for PtFe/CNT annealed at 650 °C.

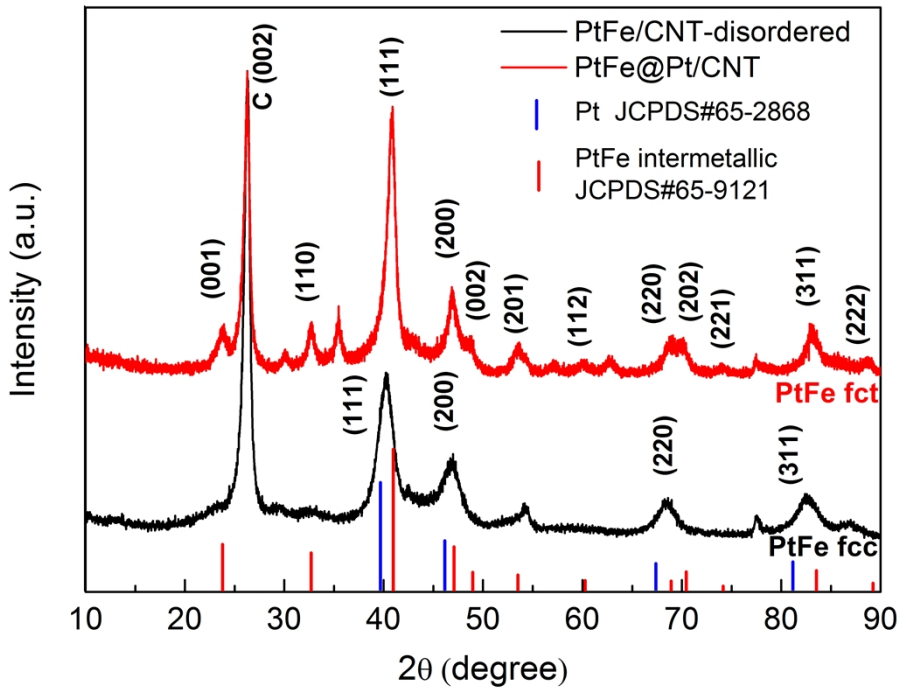

Fig. S2 XRD patterns of PtFe/CNT-disordered and PtFe@Pt/CNT electrocatalyst

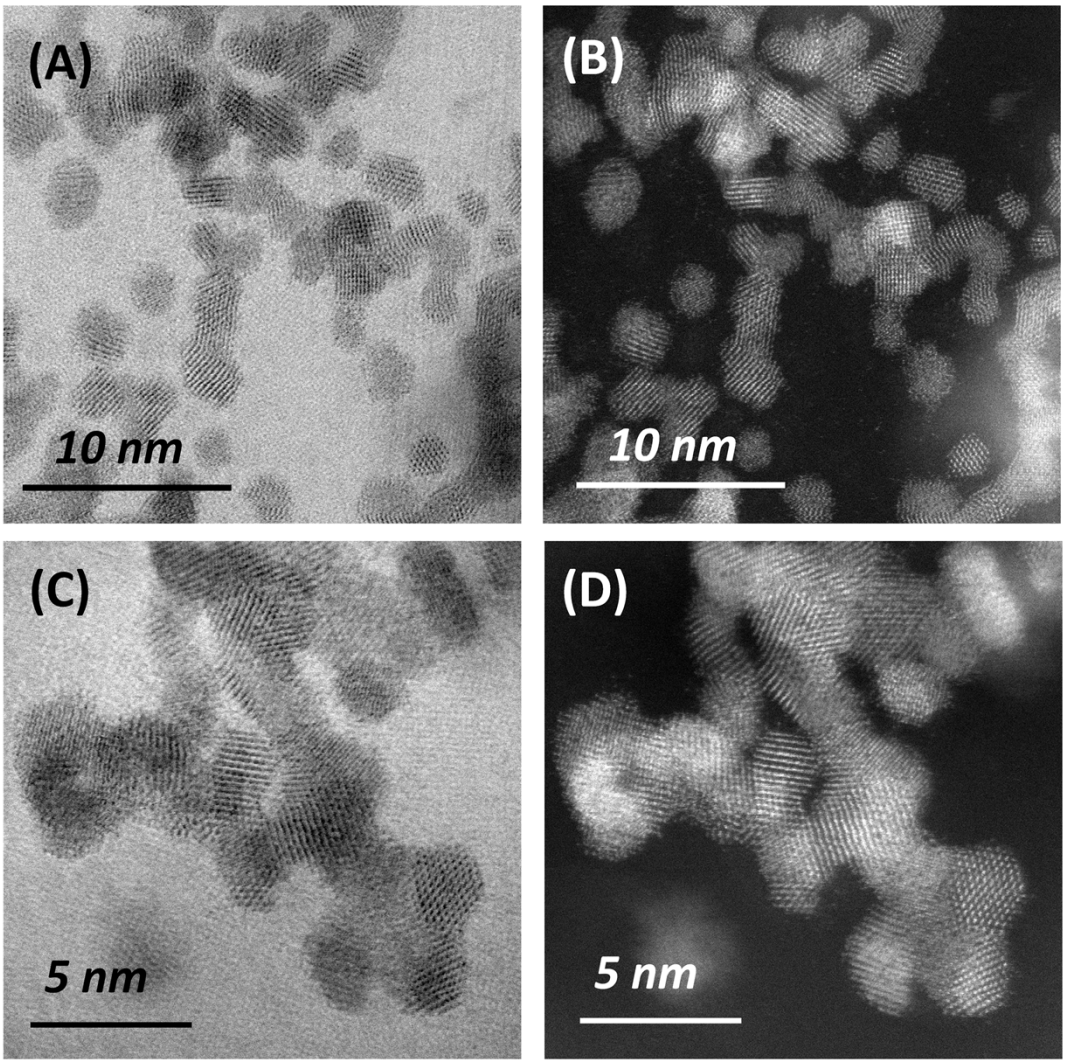

Fig. S3 High-angle annular-dark-field scanning transmission electron microscope (HAADF-STEM) images of PtFe/CNT annealed at 350 °C (A) (C) Bright-field image (B) (D) annular dark-field image

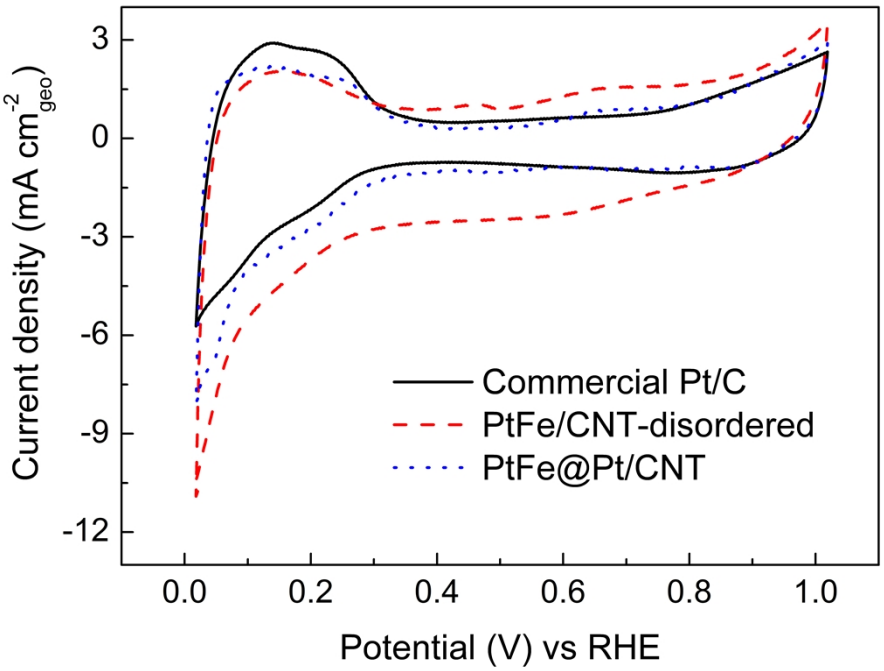

Fig. S4 Cyclic voltammetry curves of the commercial Pt/C, PtFe/CNT-disordered and PtFe@Pt/CNT electrocatalysts recorded in 0.1 mol/L $HClO_4$ at sweep rate of 50 mV/s

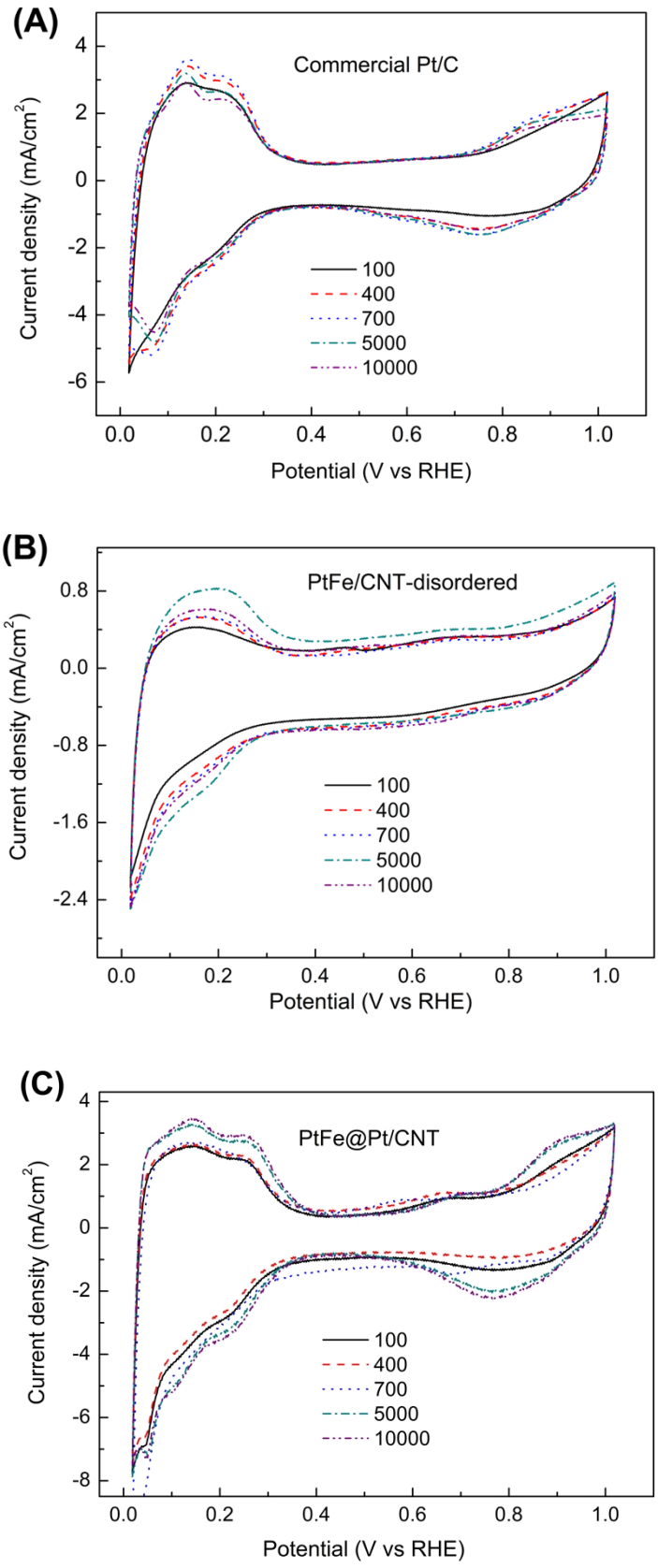

Fig. S5 Cyclic voltammetry curves of the (A) commercial Pt/C, (B) PtFe/CNT-disordered and (C) PtFe@Pt/CNT electrocatalysts recorded in 0.1 mol/L $HClO_4$ at sweep rate of 50 mV/s after various numbers of cycles during the stability test.

Table S1. Comparison of ECSA, on-set and half-wave potentials measured from the ORR polarization curves

	ECSA (m^2/g)	$E_{on\text{-}set}$ (V)	$E_{half\text{-}wave}$ (V)
Commercial Pt/C	61.8	0.996	0.905
PtFe/CNT-disordered	46.7	1.002	0.894
PtFe@Pt/CNT	50.3	1.012	0.921

Table S2. Comparison of the mass and specific activities of Pt intermetallics

No.	catalyst	MA@0.9 V mA μg^{-1}_{Pt}	SA@0.9 V mA cm^{-2}_{Pt}	Reference
1	Pt_1Fe_1/C	0.15	0.05	1
2	Pt_3Fe_1/C	0.105	0.03	1
3	$Pt@Pt_3Fe_2/C$	0.228	0.155	2
4	$PtCo_3/C$	0.23	0.31	3
5	Pt_3Ni cubes	0.05	0.5	4
6	D-Pt_3Cr/C	0.057	0.076	5
7	O-Pt_3Cr/C	0.043	0.012	5
8	$Pt_{45}Ir_{55}$-400	0.21	0.45	6
9	$Pt_{45}Ir_{55}$-800	0.18	0.51	6
10	CoCuPt	0.15	0.37	7
11	PtFe@Pt/CNT	0.308	0.26	this paper

References

1. X. Li, L. An, X. Wang, F. Li, R. Zou and D. Xia, J. Mater. Chem., 2012, 22, 6047–6052.

2. S. Prabhudev, M. Bugnet, C. Bock and G. A. Botton, ACS Nano, 2013, 7, 6103–6110.

3. H. Schulenburg, E. Muller, G. Khelashvili, T. Roser, H. Bonnemann, A. Wokaun and G. G. Scherer, J. Phys. Chem. C, 2009, 113, 4069–4077.

4. J. Zhang, H. Yang, J. Fang and S. Zou, Nano Lett., 2010, 10, 638–644.

5. L. Zou, J. Li, T. Yuan, Y. Zhou, X. Li and H. Yang, Nanoscale, 2014, 6, 10686–10692.

6. R. Loukrakpam, S. Shan, V. Petkov, L. Yang, J. Luo and C. Zhong, J. Phys. Chem. C, 2013, 117, 20715–20721.

7. J. B. Wu, Z. M. Peng, and H. Yang, Phil. Trans. R. Soc.A, 2010, 368, 4261–4274.