Supporting information for

1D Alloy Ultrafine Pt-Fe Nanowires as Efficient Electrocatalysts for Alcohol Electrooxidation in alkaline media

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Experimental Section

Chemicals

Platinum(II) acetylacetonate ($Pt(acac)_2$, reagent grade, 97%), Iron(II) acetate ($Fe(Ac)_2$, reagent grade, 95%), Tungsten carbonyl ($W(CO)_6$, reagent grade, 99%), oleylamine ($CH_3(CH_2)_7CH=CH(CH_2)_7CH_2NH_2$, OAm, 68- 70%) and 1-octadecene ($C_{18}H_{36}$, ODE, reagent grade, 90%) were all purchased from Sigma-Aldrich. N-Hexadecyltrimethylammonium Chloride ($CH_3(CH_2)_{15}N(Cl)(CH_3)_3$, CTAC, >97.0%) and Phloroglucinol ($C_6H_6O_3$, ≥99%) were purchased from Aladdin. Glucose ($C_6H_{12}O_6$, reagent grade, 97%) and ascorbic acid ($C_6H_8O_6$, AA, reagent grade, 99%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The commercial Pt/C (20 wt%, 3 nm Pt nanoparticles) was purchased from Johnson Matthey Corporation. All the chemicals were used as received without further purification. The water (18 MΩ/cm) used in all experiments was prepared by passing through an ultra-pure purification system (Aqua Solutions).

Preparation of ultrafine Pt_3Fe, Pt_2Fe and Pt_4Fe nanowires (NWs):

In a typical preparation of ultrafine Pt_3Fe NWs, $Pt(acac)_2$ (10mg), $Fe(Ac)_2$ (1.4 mg), $W(CO)_6$ (5 mg), glucose (50 mg), CTAC (32 mg), 3 mL oleylamine and 2 mL ODE were added into a glass vial (volume: 30 mL). After the vial had been capped, the mixture was ultrasonicated for 0.5 h. The resulting homogeneous mixture was then heated from room temperature to 180 °C and maintained at 180 °C for 5 h in an oil bath. The products were collected by centrifugation and washed three times with cyclohexane/ethanol mixture. The preparation of ultrafine Pt_2Fe NWs and Pt_4Fe NWs were achieved by changing the amounts of $Fe(Ac)_2$ to 2.1 mg and 1 mg, respectively, while keeping the other parameters the same.

Preparation of ultrafine Pt_3Fe NWs/C, Pt_2Fe NWs/C and Pt_4Fe NWs/C:

The products of ultrafine Pt_3Fe NWs, Pt_2Fe NWs and Pt_4Fe NWs were collected by centrifugation and washed three times with cyclohexane/ethanol mixture. Then, we loaded the catalysts on carbon black (Vulcan XC72R carbon, C) by sonication and washed with ethanol at room temperature twice. Finally, the sample is centrifuged and dried.

Characterizations

The samples were prepared by dropping cyclohexane dispersion of samples onto carbon-coated copper transmission electron microscopy (TEM) grids using pipettes and dried under ambient condition. Low-magnification TEM was conducted on a HITACHI HT7700 TEM at an acceleration voltage of 120 kV. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was conducted on a FEI Tecnai F20 TEM at an accelerating voltage of 200 kV. PXRD pattern was collected on X'Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu Kα X-ray source (λ = 1.540598 Å). X-ray photoelectron spectroscopy spectra (XPS) were conducted on a Thermo Scientific ESCALAB 250 XI X-ray photoelectron spectrometer. The concentration of all the catalysts was determined by the ICP-AES (710-ES, Varian).

Ethylene glycol oxidation reaction (EGOR) and glycerol oxidation reaction (GOR) measurements

A three-electrode cell was used for the electrochemical measurements. A glassy-carbon electrode (GCE) (diameter: 3 mm, area: 0.07 cm^2) from Pine Instruments was used as the working electrode, a saturated calomel electrode (SCE) was used as the reference electrode and a Pt wire was used as the counter electrode, respectively. To prepare the catalyst-coated working electrode, the catalyst was dispersed in a mixture containing isopropanol and Nafion (5%) to form a 0.40 mg_{Pt}/mL dispersion. 5 μL isopropanol dispersion of ultrafine Pt_3Fe NWs, Pt_2Fe NWs or Pt_4Fe NWs on C (0.40 mg_{Pt}/mL) was deposited on a glassy carbon electrode to obtain the working electrode after the solvent was dried naturally. We have conducted the CV measurements of ultrafine Pt-Fe NWs and commercial Pt/C in the 1 M KOH solution. EGOR was conducted in 1.0 M KOH + 1.0 M EG solution. GOR was conducted in 1.0 M KOH + 1.0 M glycerol solution. The scan rates for EGOR and GOR were 50 mV/s. The durability test was performed at room temperature by applying the CV at sweep rate of 50 mV/s for 250 cycles. All electrochemical experiments were performed at room temperature. For comparison, the commercial Pt/C was used as the baseline catalyst, and the same procedure as described above was applied to conduct the electrochemical measurements. Current-time (I-t) curves and electrochemical impedance spectroscopy (EIS) conducted by electrochemical work station. For detailed information, the EIS measurements were taken in frequency range of 100/kHz Hz at 0.25 V with an AC amplitude of 5 mV carried out on CHI 760E No.413187 electrochemical workstation fabricated by Chen Hua Instrumental Corp (Shanghai, China).

Supporting Figures and Table

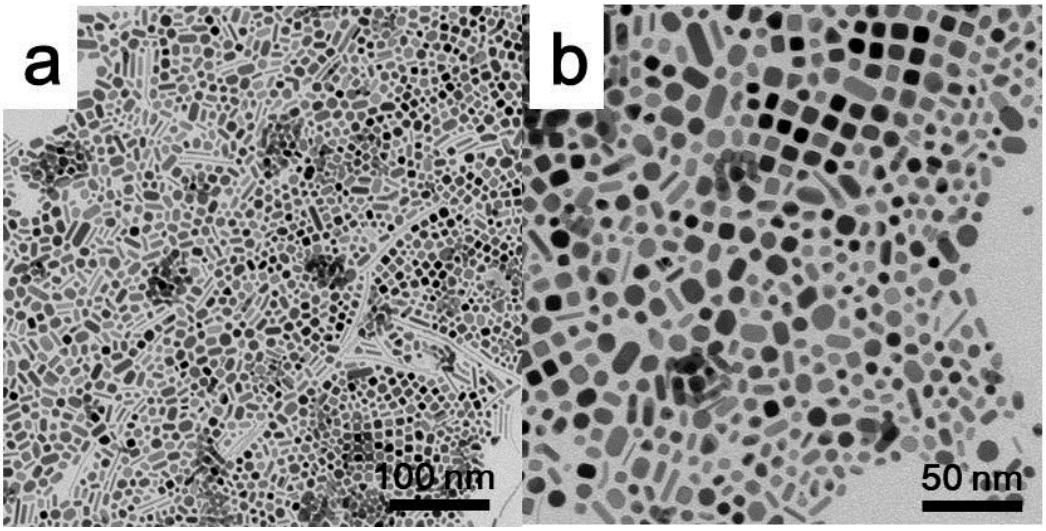

Fig. S1 (a, b) TEM images of the products with the same reaction conditions as that of ultrafine Pt_3Fe NWs but in absence of $Fe(Ac)_2$.

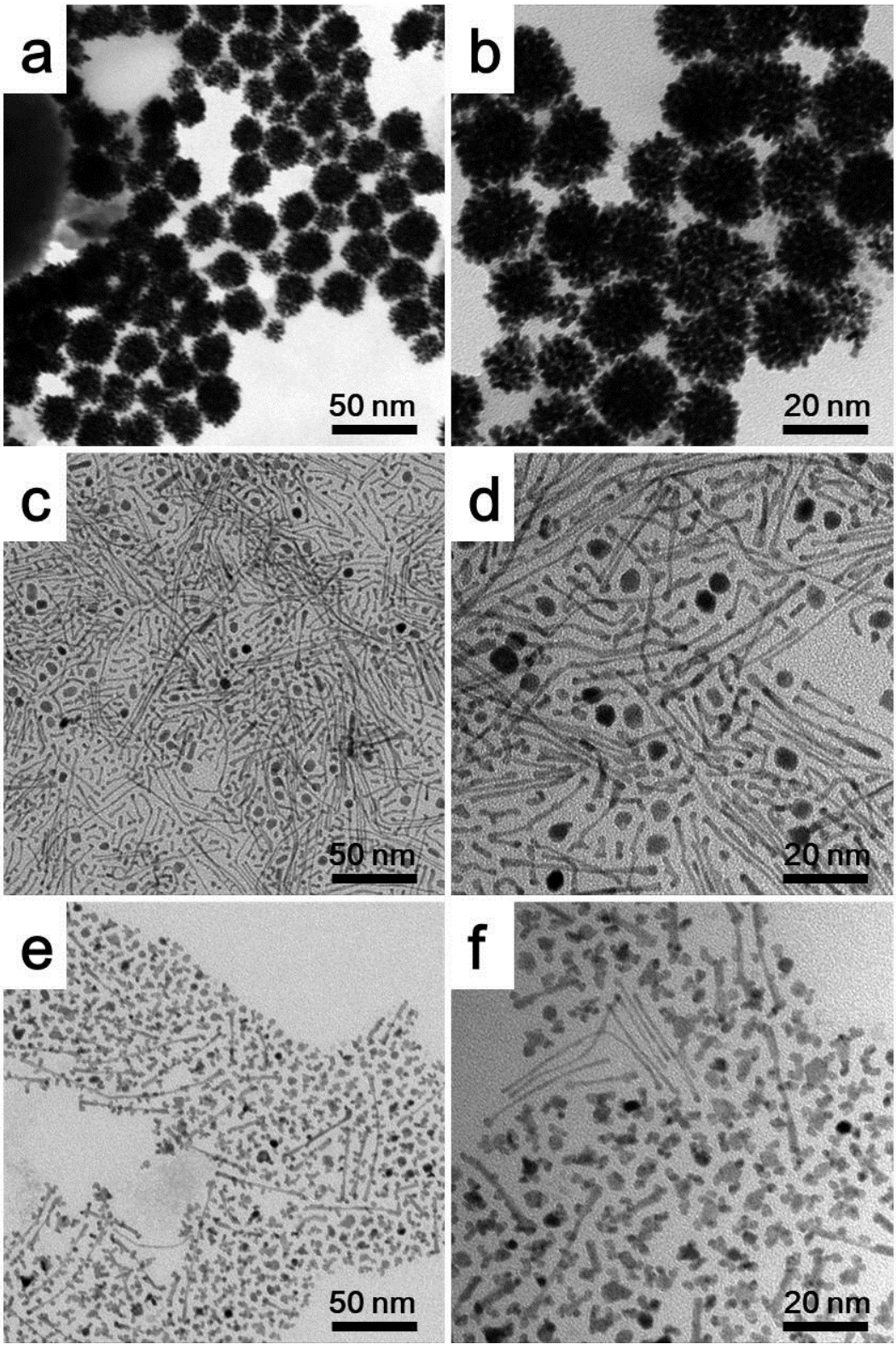

Fig. S2 TEM images of the products with the same reaction conditions as that of ultrafine Pt_3Fe NWs except the use of (a, b) 0 mg $W(CO)_6$, (c, d) 0 mg glucose and (e, f) 0 mg CTAC.

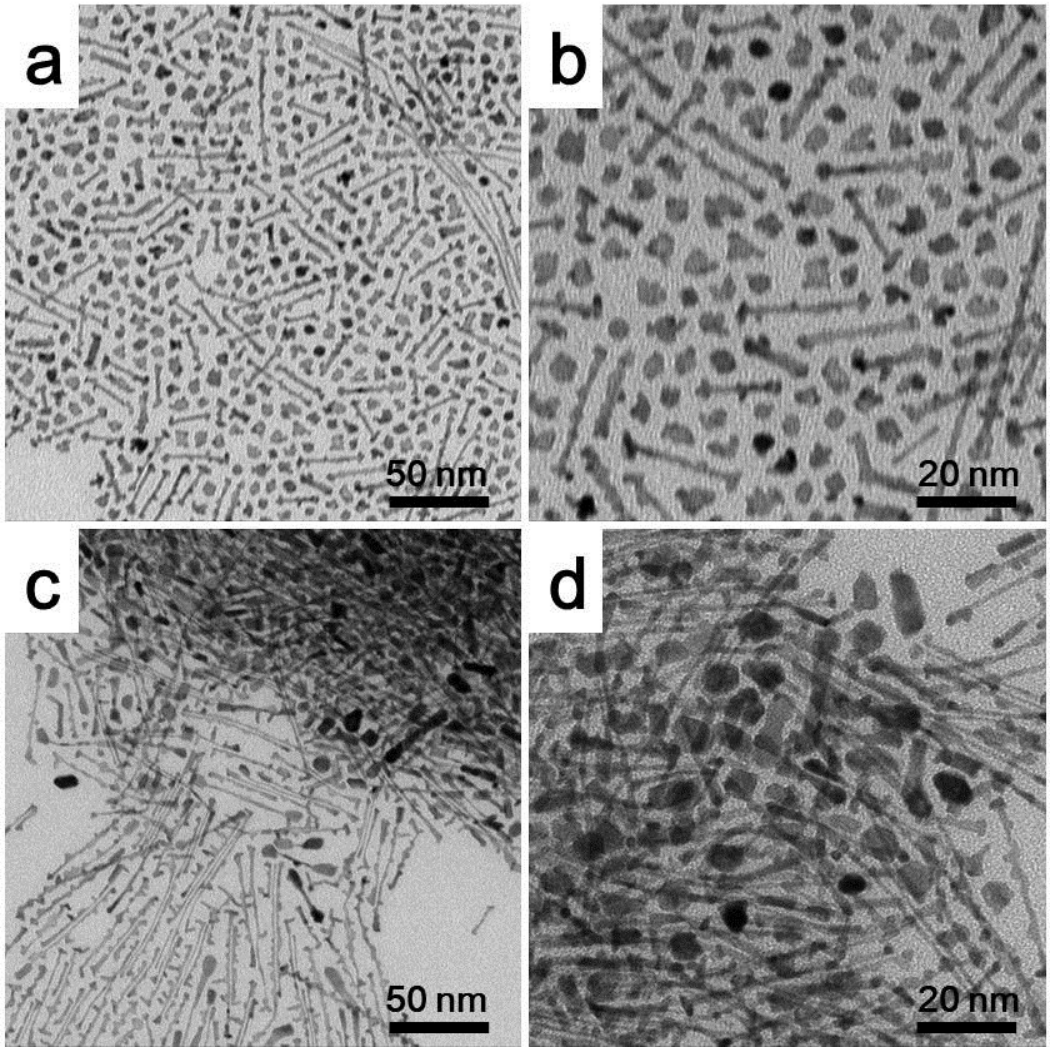

Fig. S3 TEM images of the products with the same reaction conditions as that of ultrafine Pt_3Fe NWs but changing glucose into (a, b) 50 mg AA, (c, d) 50 mg phloroglucinol.

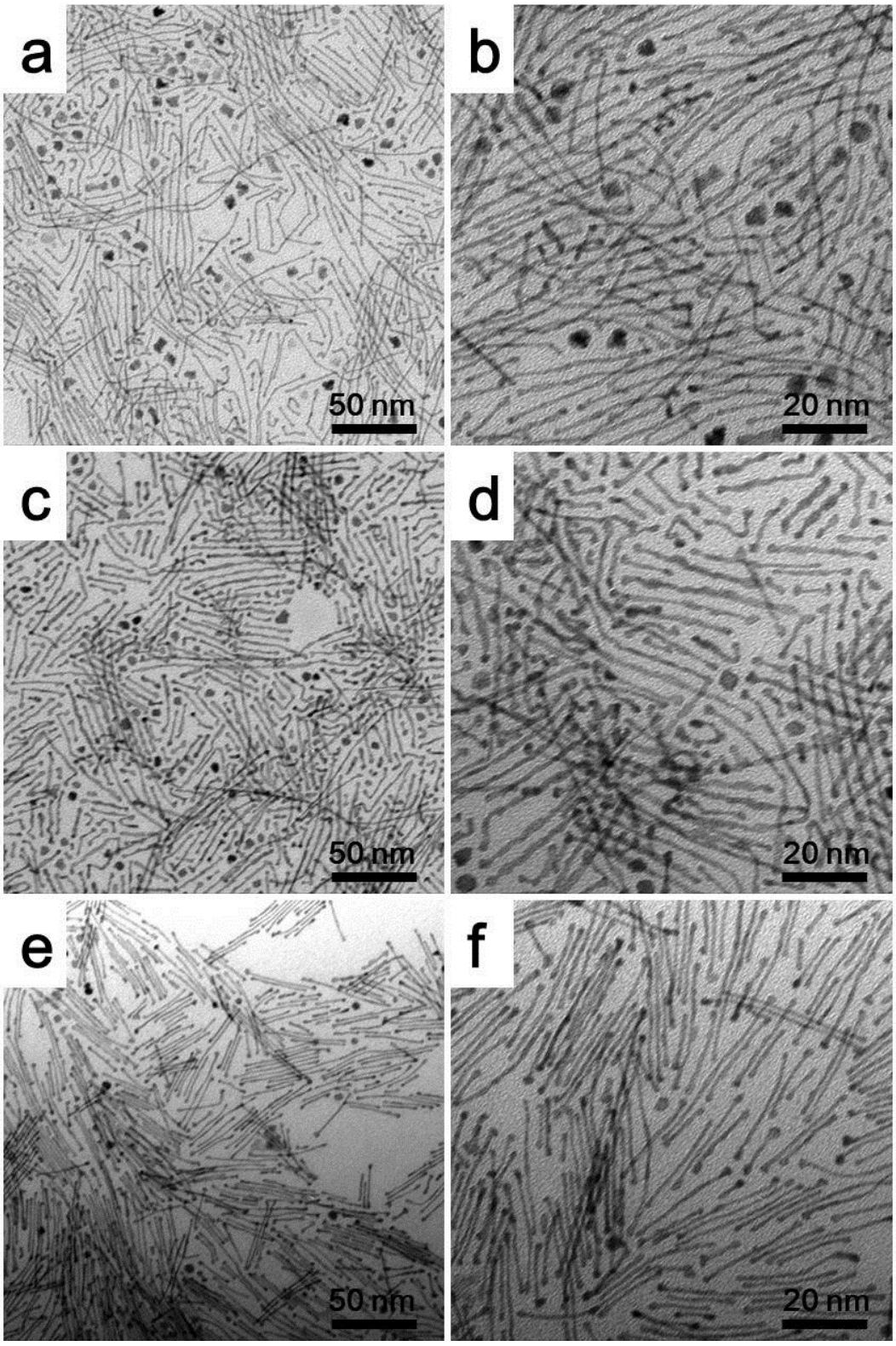

Fig. S4 TEM images of the products with the same reaction conditions as that of ultrafine Pt_3Fe NWs except the use of (a, b) 5 mL OAm, (c, d) 4 mL OAm : 1mL ODE and (e, f) 2 mL OAm : 3mL ODE.

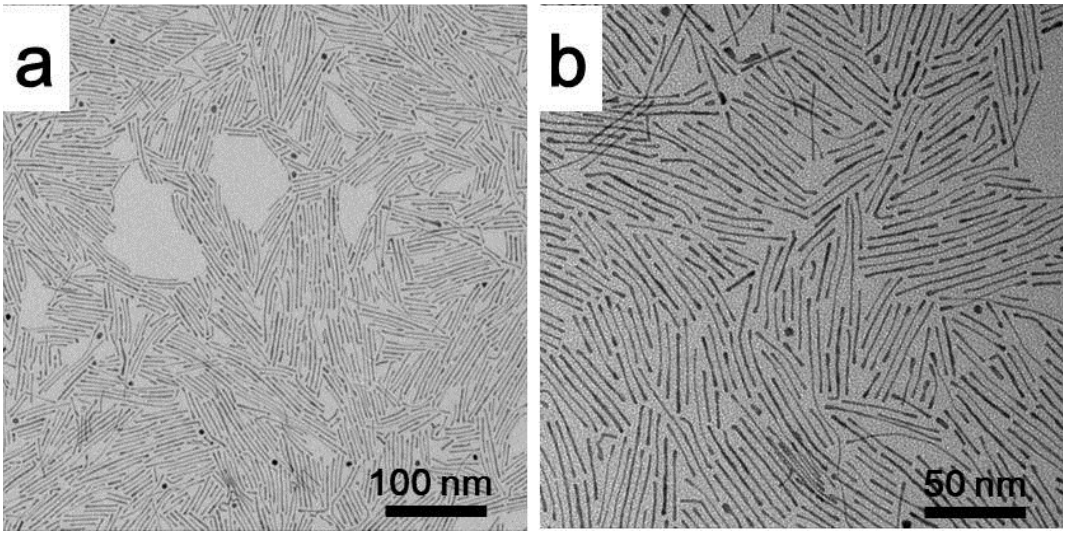

Fig. S5 (a, b) Additional TEM images of the ultrafine Pt_3Fe NWs.

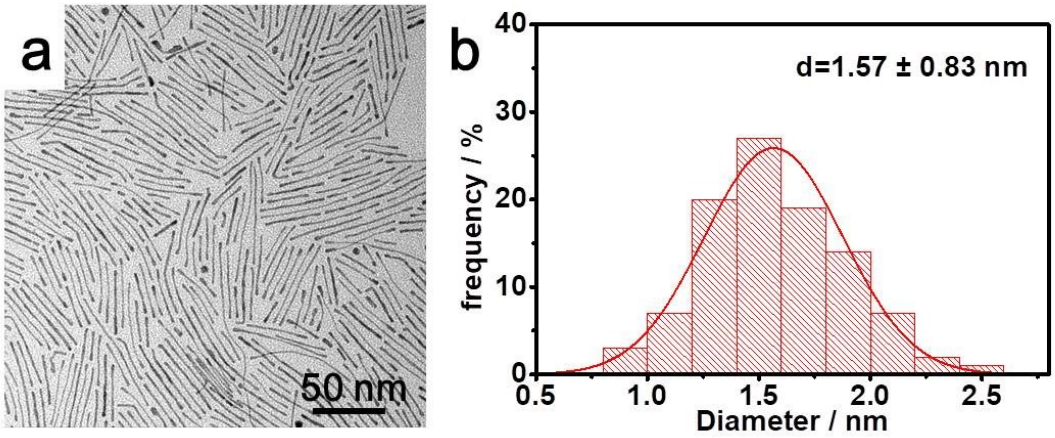

Fig. S6 (a) TEM image and (b) the diameter distribution of ultrafine Pt_3Fe NWs.

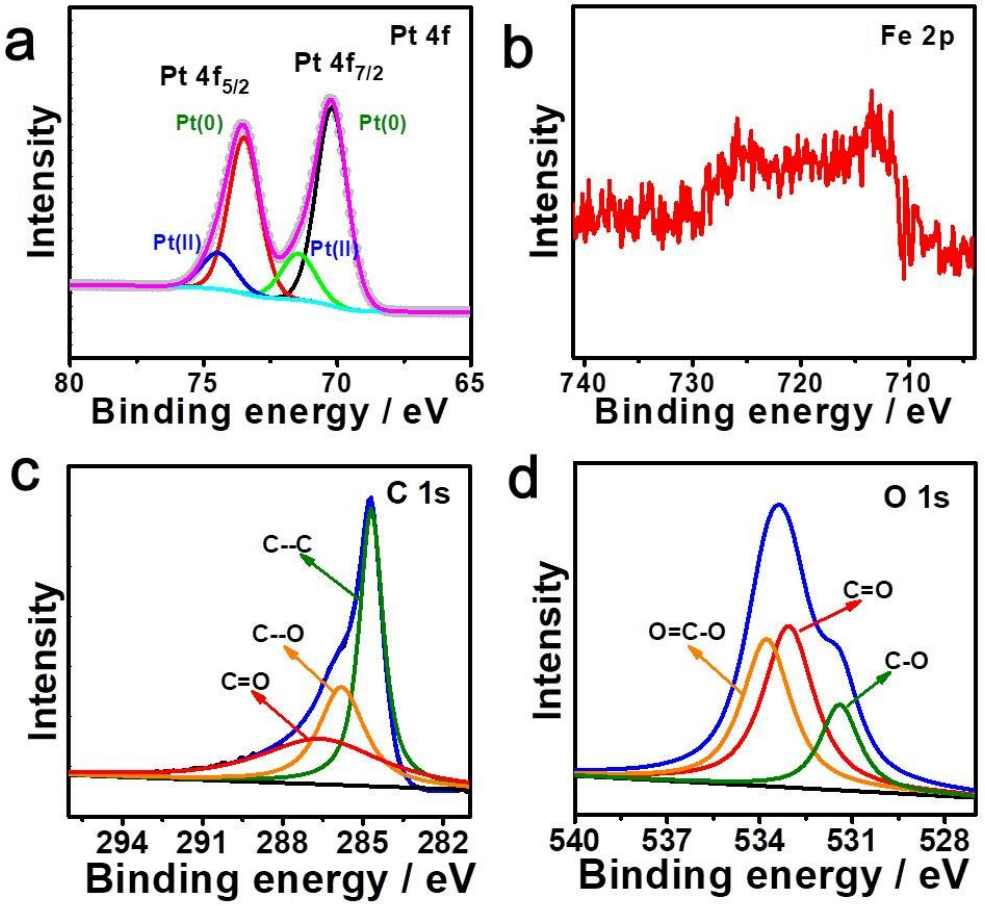

Fig. S7 XPS spectra of ultrafine Pt_3Fe NWs. (A) Pt 4f, (B) Fe 2p, (C) C 1s, (D) O 1s XPS spectra, respectively.

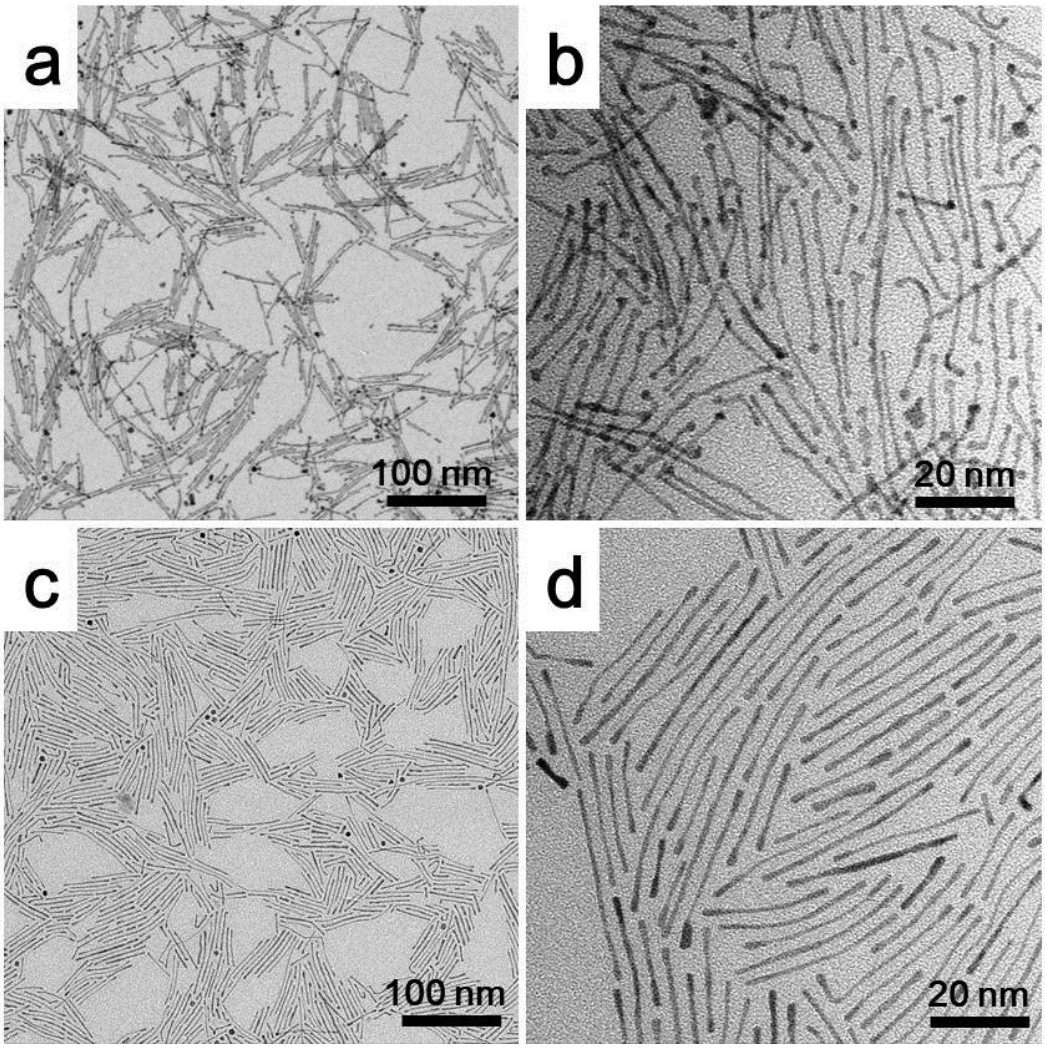

Fig. S8 Additional TEM images of (a, b) the ultrafine Pt_2Fe NWs and (c, d) the ultrafine Pt_4Fe NWs.

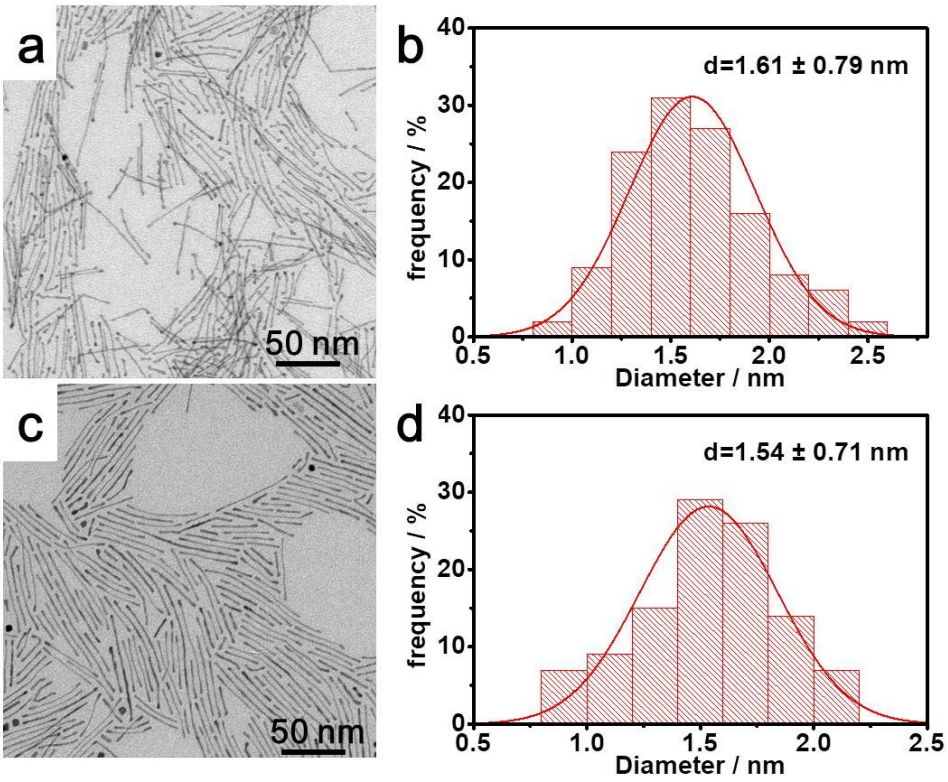

Fig. S9 (a, b) TEM image and diameter distribution of Pt_2Fe NWs, (c, d) TEM image and diameter distribution of Pt_4Fe NWs.

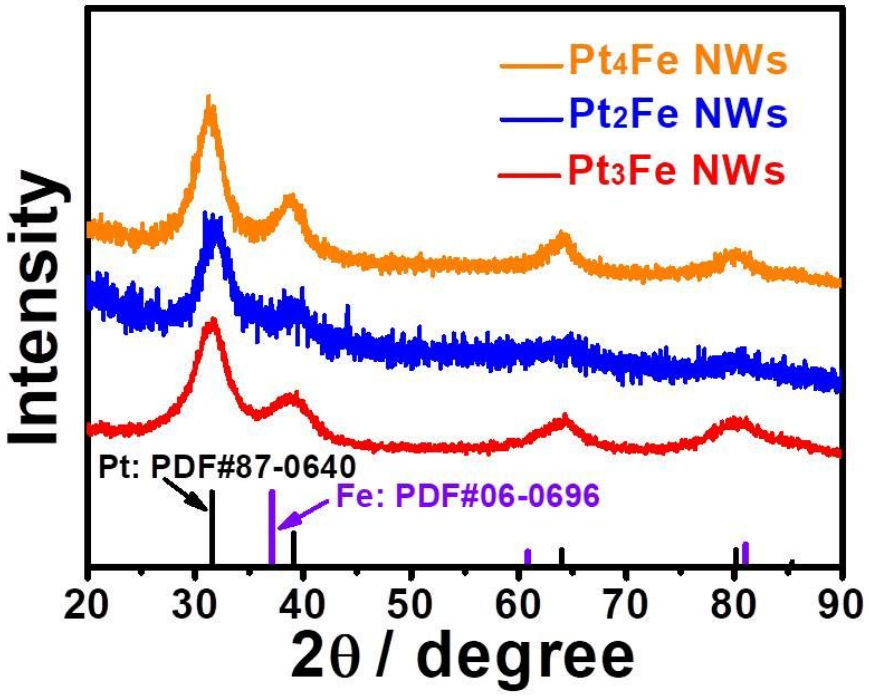

Fig. S10 XRD patterns of ultrathin Pt_3Fe NWs, Pt_2Fe NWs, Pt_4Fe NWs.

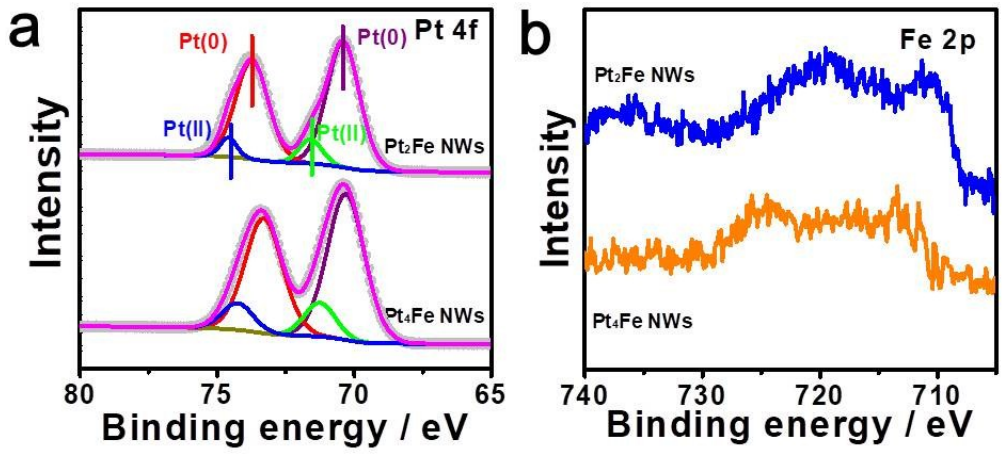

Fig. S11 XPS spectra of ultrafine Pt_2Fe NWs and ultrafine Pt_4Fe NWs. (A) Pt 4f, (B) Fe 2p.

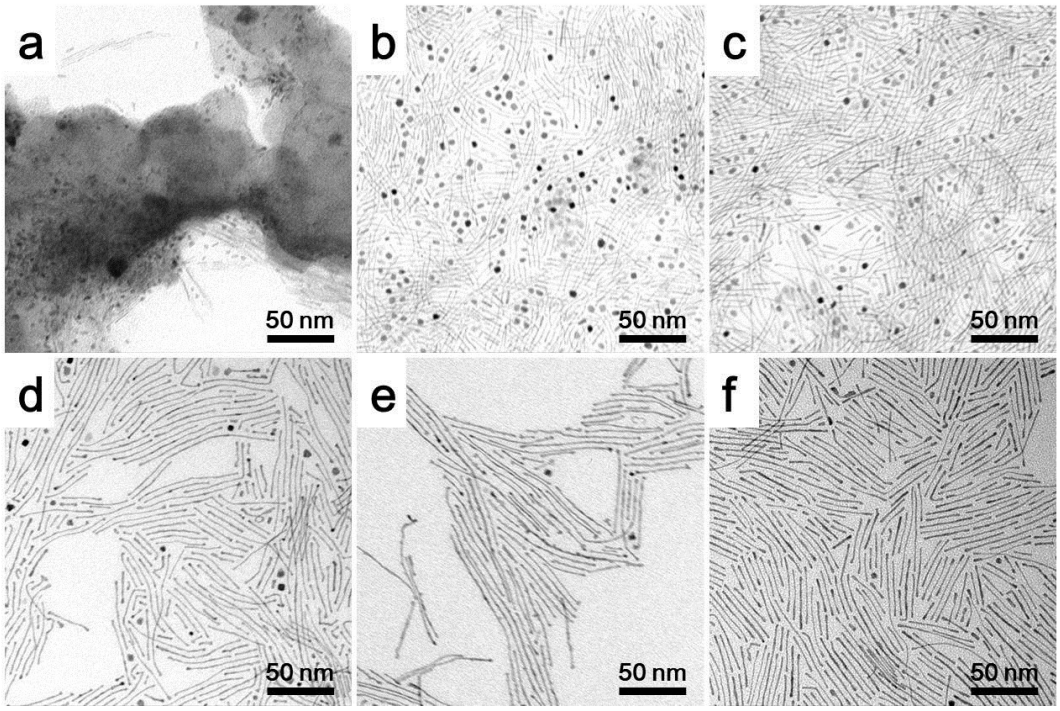

Fig. S12 Representative TEM images of the ultrafine Pt_3Fe NWs intermediates obtained after the reaction have been processed for (a) 10 min, (b) 30 min, (c) 1 h, (d) 2 h, (e) 3 h and (f) 5 h.

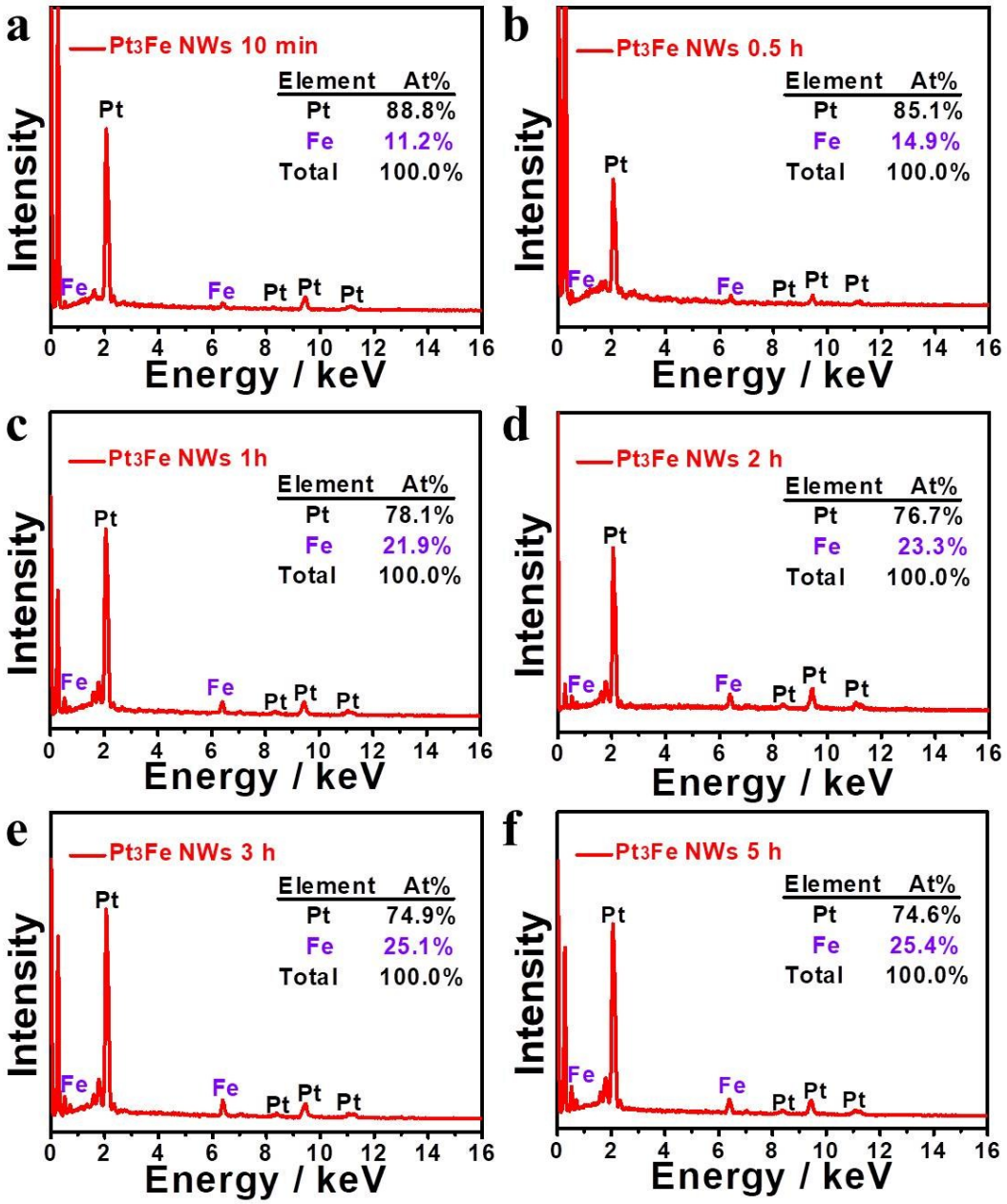

Fig. S13 SEM-EDX spectrum of the ultrafine Pt_3Fe NWs intermediates obtained after the reaction have been processed for (a) 10 min, (b) 30 min, (c) 1 h, (d) 2 h, (e) 3 h and (f) 5 h.

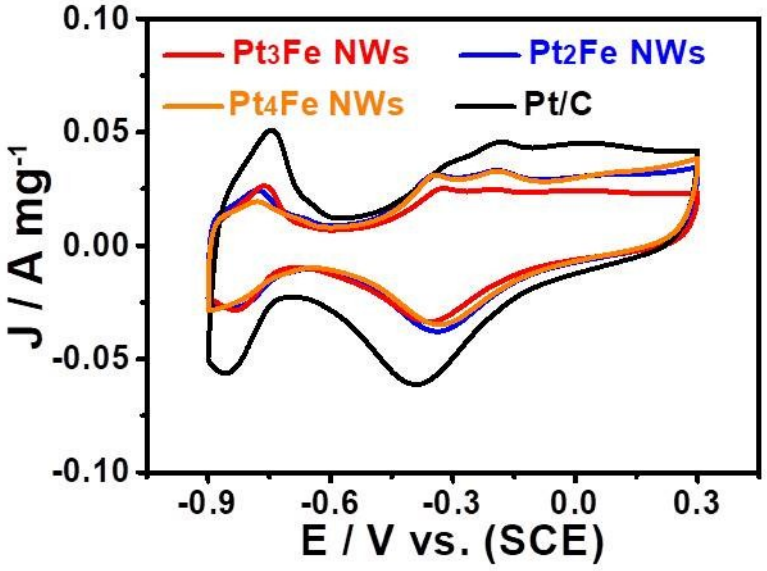

Fig. S14 The CV curves of ultrafine Pt_3Fe NWs, Pt_2Fe NWs, Pt_4Fe NWs and commercial Pt/C in 1 M KOH solution.

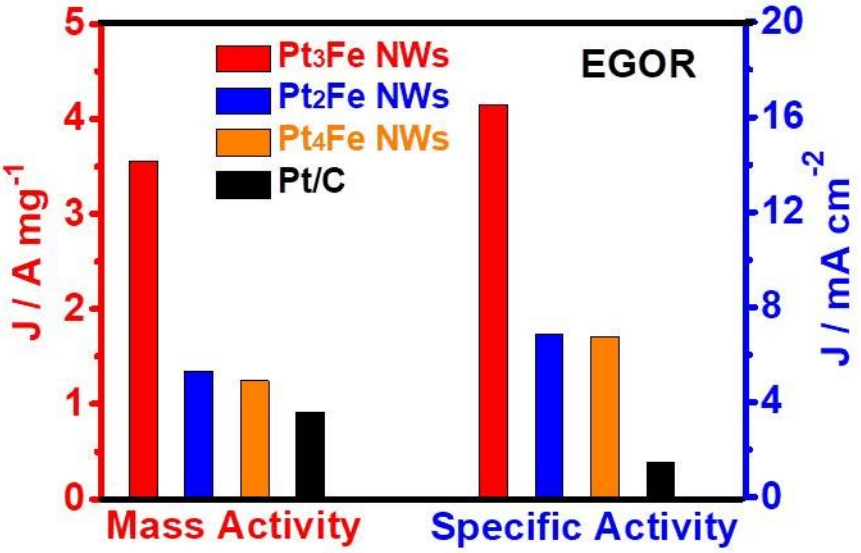

Fig. S15 The mass and specific activities of different catalysts for EGOR.

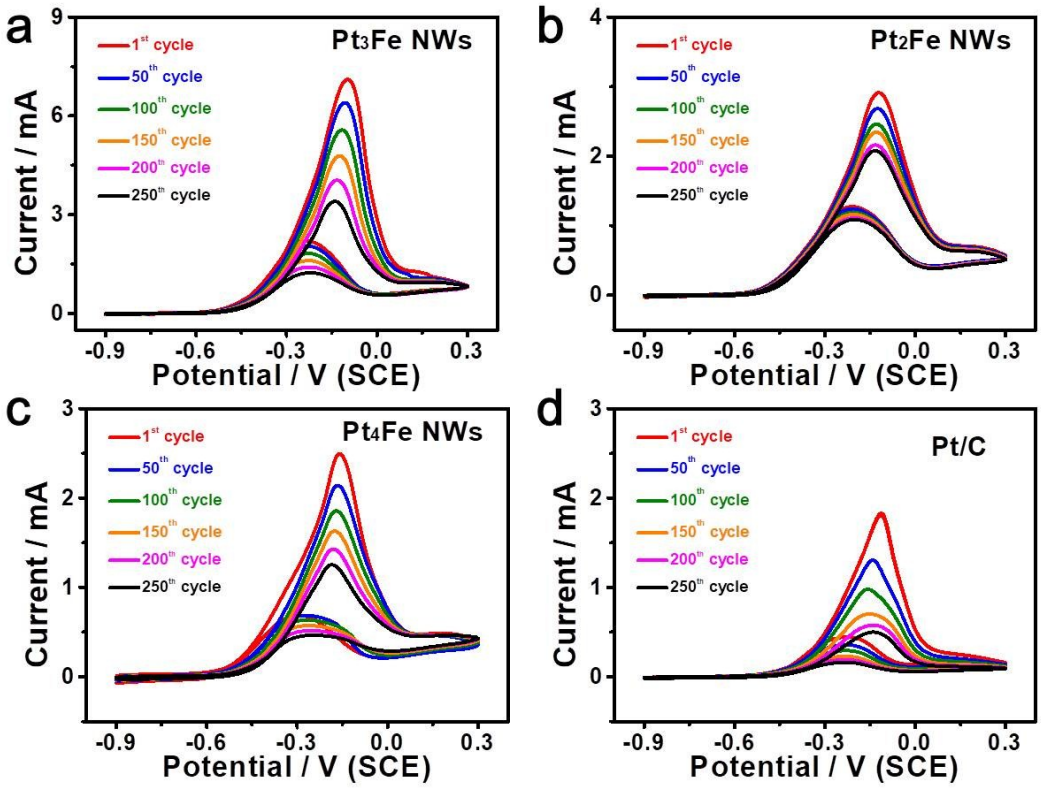

Fig. S16 CV curves of (a) ultrafine Pt_3Fe NWs, (b) ultrafine Pt_2Fe NWs, (c) ultrafine Pt_4Fe NWs and (d) Pt/C for EGOR for 250 cycles. Potential CV was scanned in 1 M KOH and 1 M EG solution at 50 mV s^{-1}.

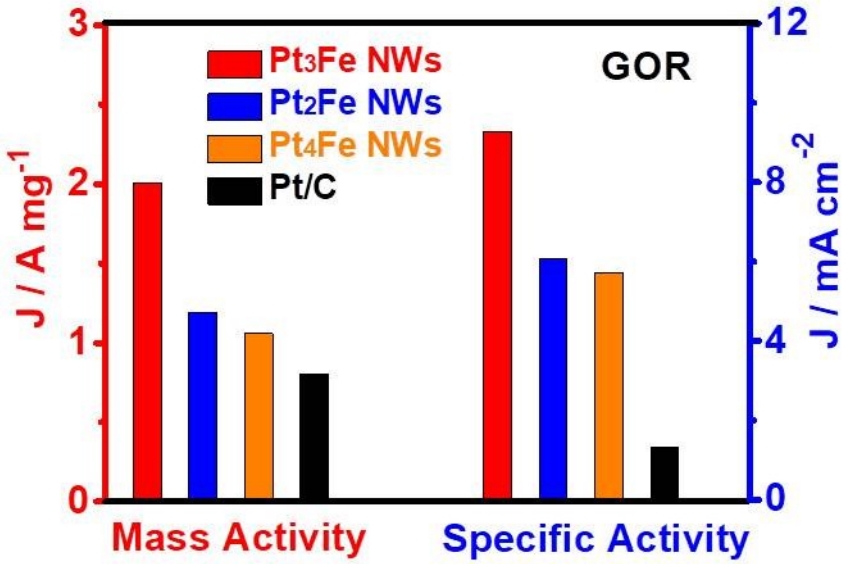

Fig. S17 The mass and specific activities of different catalysts for GOR.

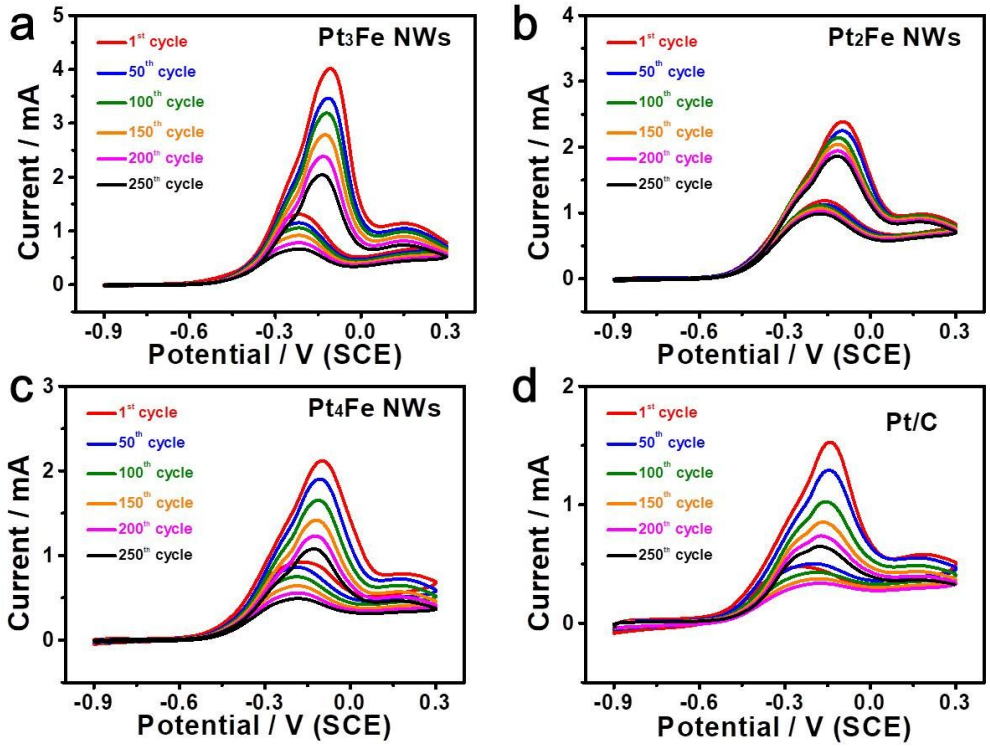

Fig. S18 CV curves of (a) ultrafine Pt_3Fe NWs, (b) ultrafine Pt_2Fe NWs, (c) ultrafine Pt_4Fe NWs and (d) Pt/C for GOR for 250 cycles. Potential CV was scanned in 1 M KOH and 1 M glycerol at 50 mV s^{-1}.

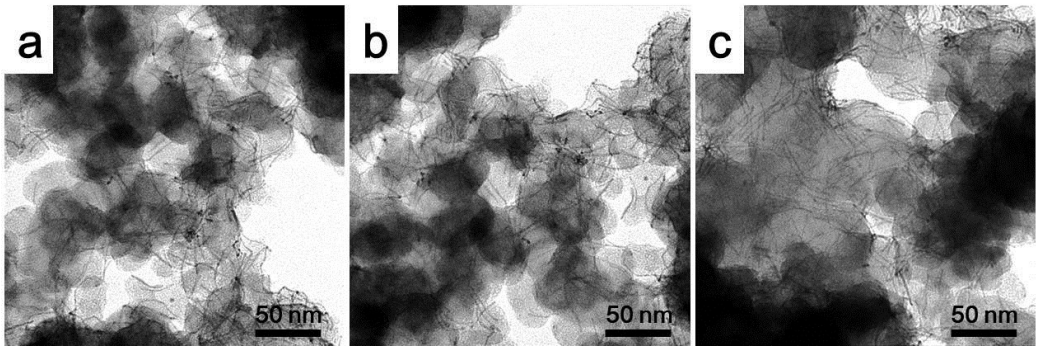

Fig. S19 Representative TEM images of (a) ultrafine Pt_3Fe NWs, (b) ultrafine Pt_2Fe NWs and (c) ultrafine Pt_4Fe NWs catalysts before electrochemical durability test.

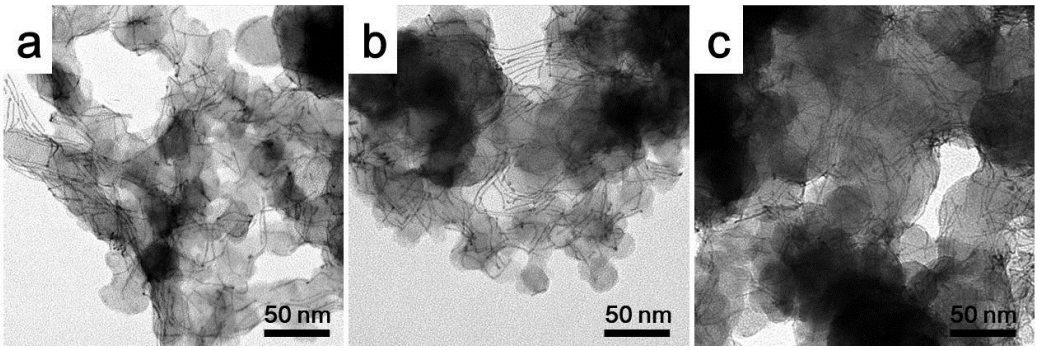

Fig. S20 Representative TEM images of (a) ultrafine Pt_3Fe NWs, (b) ultrafine Pt_2Fe NWs and (c) ultrafine Pt_4Fe NWs catalysts after electrochemical durability test.

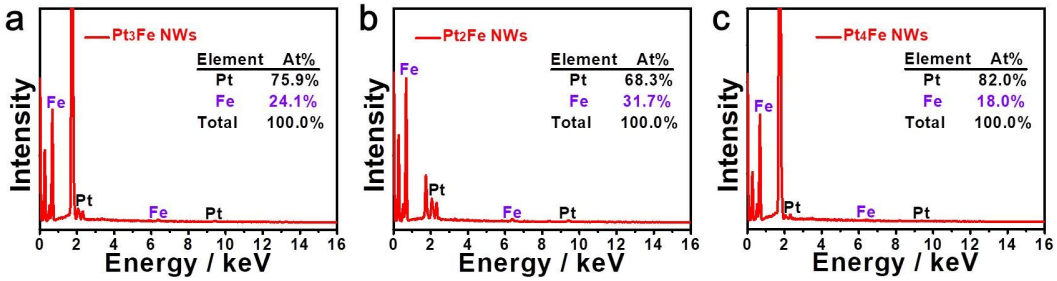

Fig. S21 SEM-EDX spectrum of (a) ultrafine Pt_3Fe NWs, (b) ultrafine Pt_2Fe NWs and (c) ultrafine Pt_4Fe NWs catalysts after electrochemical durability test.

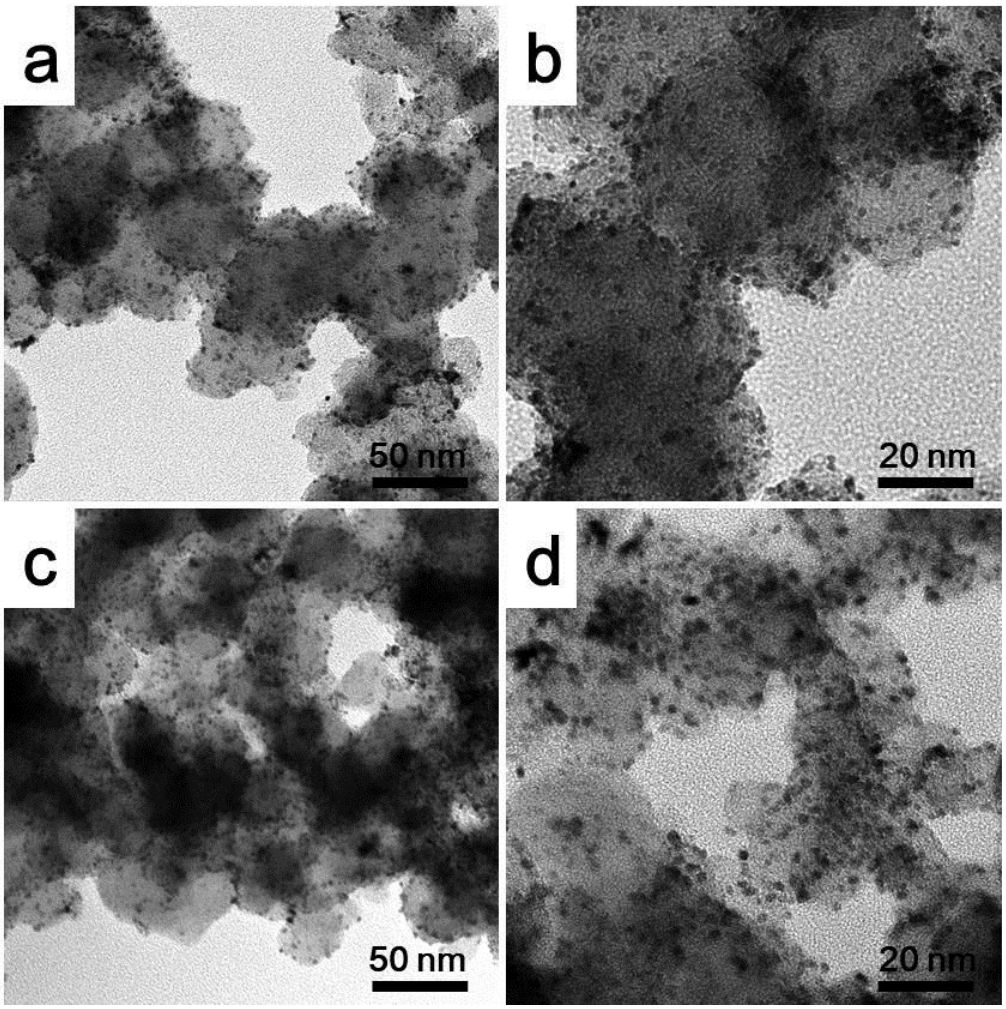

Fig. S22 TEM images of Pt/C (a, b) before and (c, d) after 250 cycles in 1 M KOH containing 1 M glycerol at 50 mV s^{-1}.

Table S1 Comparison of ultrafine Pt_3Fe NWs catalysts with other Pt-based electrocatalysts for the EGOR.

Catalysts	Peak currents from CV curves		Electrolytes	References
	Jm (A/mg_{Pt})	*Js* (mA/cm^2)		
Ultrafine Pt_3Fe NWs	**3.56**	**16.53**	**1 M KOH + 1 M EG**	**This Work**
$PtNi_{0.67}Pb_{0.26}$ NWs/C	0.42	0.65	0.1 M $HClO_4$ + 0.2 M EG	*J. Mater. Chem. A* 2017, **5**, 18977-18983
PtRu alloy	3.052	~	1.0 M KOH + 1.0 M EG	*Int. J. Hydrogen Energy* 2017, **42**, 20720-20728
$Pt_{84}Ru_{16}$	~	2.1	1 M KOH + 0.1 M EG	*Electrochim. Acta* **2012**, *66*, 295.
$Pt_{96}Sn_4$	~	1.4		
$Pt_{88}Ru_6Sn_6$	~	1.3		
Pt-Sn Nanocrystals/CNT	0.22	~	0.5 M H_2SO_4 + 1 M EG	*Int. J. Hydrogen Energy* 2011, **36**, 3313-3321
$Pt_{4.5}Pb$ NWs	0.73	0.30	0.1M $HClO_4$ + 0.5 M EG	*Small* 2016, **12**, 4464-4470
$Pt_{5.7}Pb$ NWs	0.63	0.22		