Supporting Information for

Novel Networked Wicker-like PtFe Nanowires with Branch-rich Exteriors for Efficient Electrocatalysis

Yangping Zhang,‡ Fei Gao,‡ Tongxin Song, Cheng Wang, Chunyan Chen, and Yukou Du*

[a] *College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P.R. China.*

** Corresponding author: E-mail: duyk@suda.edu.cn (Y. Du)*

Yangping Zhang and Fei Gao contributed equally to this manuscript.

1. Experimental Section

1.1 Materials and reagents

Platinum(II) acetylacetonate ($Pt(acac)_2$, 97%), and iron(II) acetate ($Fe(Ac)_2$, reagent grade, 95%) were purchased from Shanghai Macklin Biochemical Co. Ltd. Oleylamine (OAm, 90%), N-Hexadecyltrimethylammonium Chloride ($CH_3(CH_2)_{15}N(Cl)(CH_3)_3$, CTAC, >97.0%), Phloroglucinol anhydrous ($C_6H_6O_3$, ≥99%), Tungsten carbonyl ($W(CO)_6$, 98%) were bought from Aladdin Co. Ltd. Methanol (CH_3OH, A.R. 99%), ethanol (CH_3CH_2OH, A.R. grade, 99.7%), cyclohexane (C_6H_{12}, A.R. grade, 98%) were all purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Water (H_2O, 18 MΩ/cm) used in all experiments was prepared by passing through an ultra-pure purification system.

1.2 Preparation of PtFe NWs.

In the typical preparation of Pt_3Fe NWs, $Pt(acac)_2$ (10 mg), $Fe(Ac)_2$ (1.4 mg), $W(CO)_6$ (5 mg), phloroglucinol anhydrous (10 mg), CTAC (32 mg), and 5 mL OAm were dissolved into a glass vial (volume: 20 mL). After capping the vial, the mixture was kept for 1 h under ultrasound condition. Subsequently, the resulting homogeneous mixture was then heated from ambient temperature to 180 °C and maintained at 180 °C for 9 h in an oil bath. The products were collected by centrifugation and washed three

times with a cyclohexane/ethanol mixture. The obtained catalyst was denoted as Pt_3Fe NWs. By changing the amount of metal precursor Fe $(Ac)_2$ to 2.2 mg and 1.1 mg, Pt_4Fe NWs and Pt_2Fe NWs were synthesized while keeping other reaction conditions same.

1.3 Characterizations

In physical characterizations, transmission electron microscope (TEM, accelerating voltage: 120 kV, HT-7700) was conducted to analyze the micromorphology of as-obtained catalysts. High resolution TEM (HRTEM, operation voltage: 200 kV, F20) technique was employed to investigate the crystal structure. The composition of catalysts was obtained by scanning electron microscope energy-dispersive X-ray spectroscopy (SEM-EDS, HITACHI S-4700, operate voltage: 15 kV). X-ray diffraction (XRD, Netherlands PANalytical) analysis was conducted on X'Pert-Pro MPD diffractometer. Furthermore, the elemental states were analyzed by X-ray photoelectron spectroscopy (XPS), which conducted on a VG Scientific ESCALab 220 XL electron spectrometer with 300 W Al Kα radiation.

1.4 Electrochemical measurements

Electrochemical tests were conducted in a three-electrode cell system. The working electrode is glassy carbon electrode (GCE, diameter: 5.0 mm), the counter electrode is platinum wire, and reference electrode is saturated calomel electrode (SCE). 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. Subsequently, the electrochemical active surface area (ECSA) of those catalysts is relative to surface active sites and could be measured by cyclic voltammetry (CV) in 0.1 M $HClO_4$ solution with the scanning rate of 50 mV s^{-1}. EOR and MOR tests were operated in 0.1 M $HClO_4$ + 0.5 M ethanol and 0.1 M $HClO_4$ + 0.5 M methanol solution, respectively. For durability tests, Chronoamperometry (CA) measurements and successive CVs for 1000 cycles of as-prepared catalysts were also conducted. All the electrochemical tests were conducted by electrochemical work station (CHI760E) produced by Chen Hua Instrumental Co., Ltd (Shanghai, China).

2. Supporting Figure and Tables

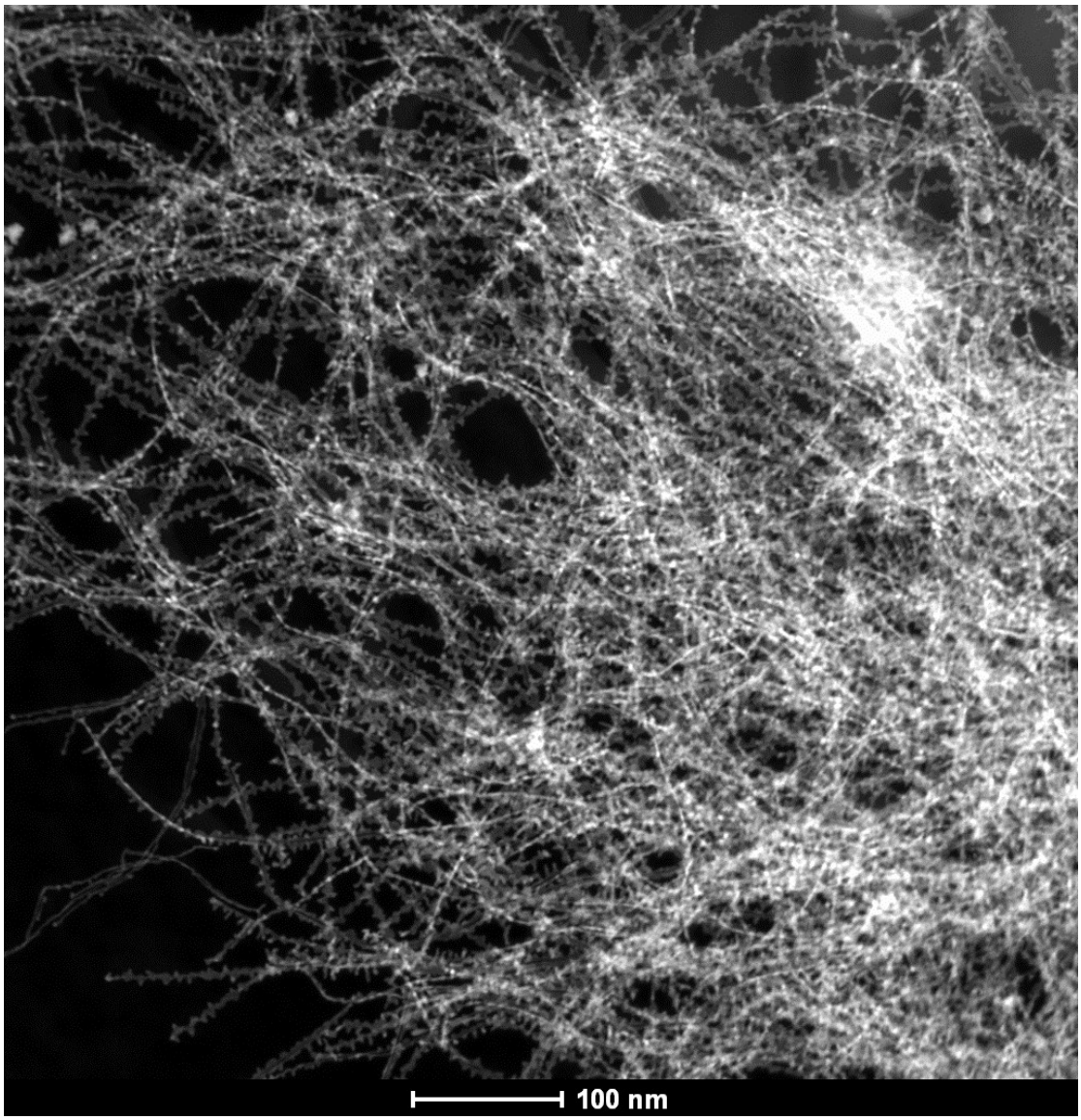

Fig. S1 Additional HAADF-STEM image of Pt_3Fe NWs.

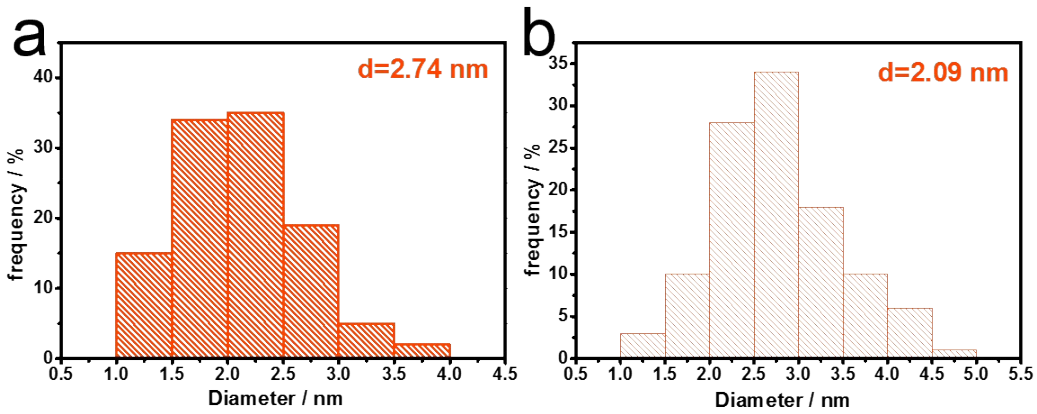

Fig. S2 Size distribution of the diameter of (a) NWs and (b) exterior branches in Pt_3Fe NWs.

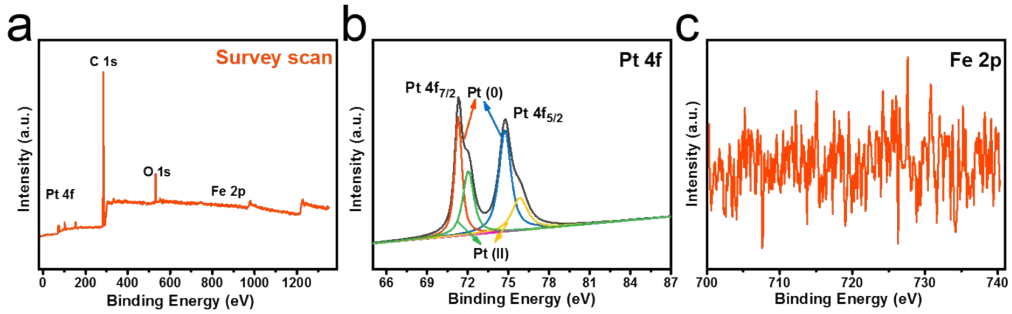

Fig. S3 XPS spectra of (a) survey scan, (b) Pt 4f, (c) Fe 2p in Pt_3Fe NWs.

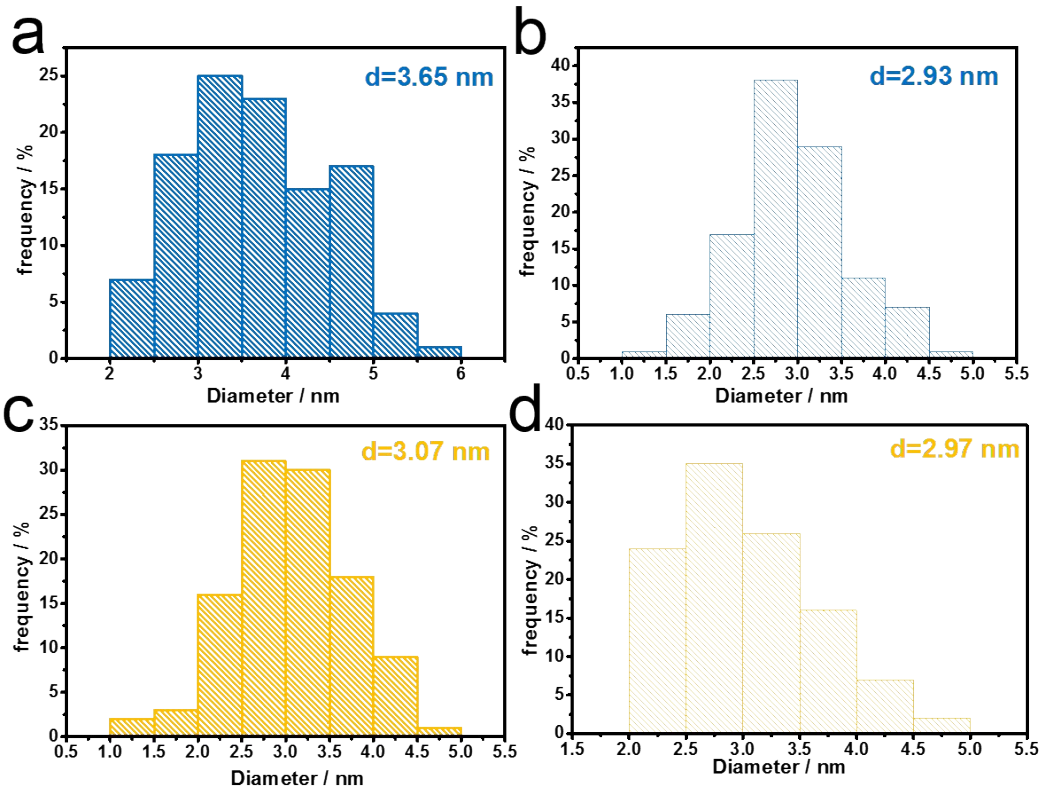

Fig. S4 Size distribution of (a) NWs and (b) exterior branches in Pt_2Fe NWs, (c) NWs and (d) exterior branches in Pt_4Fe NWs.

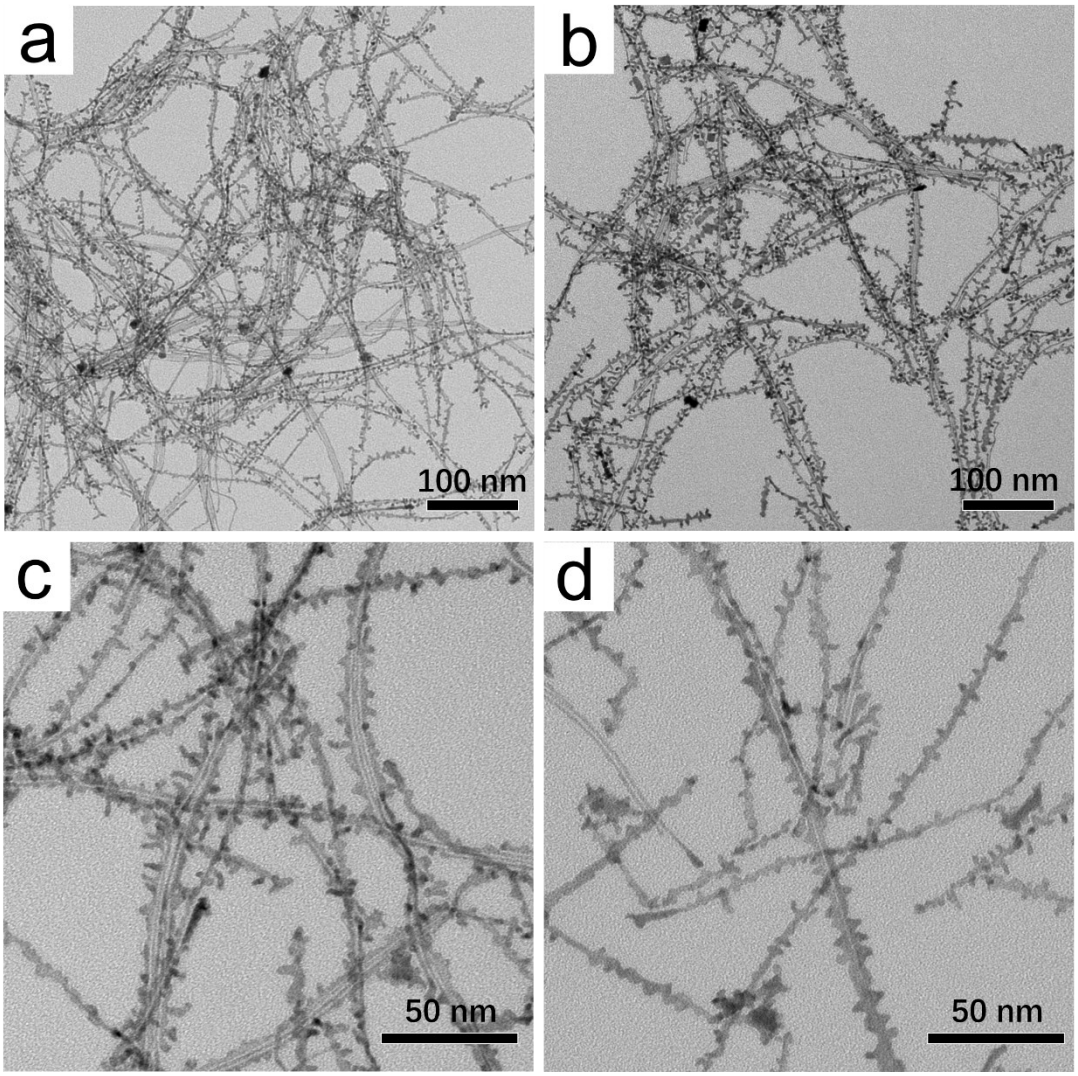

Fig. S5 Additional TEM images of (a, c) Pt_2Fe NWs and (b, d) Pt_4Fe NWs.

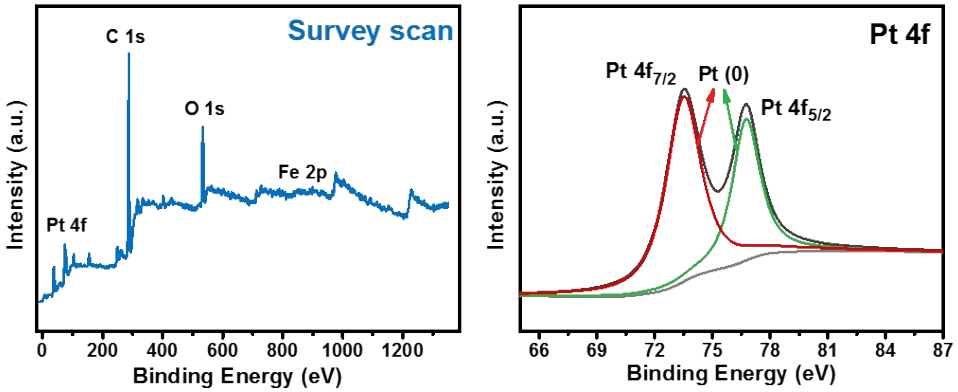

Fig. S6 XPS spectra of (a) survey scan, (b) Pt 4f in Pt_2Fe NWs.

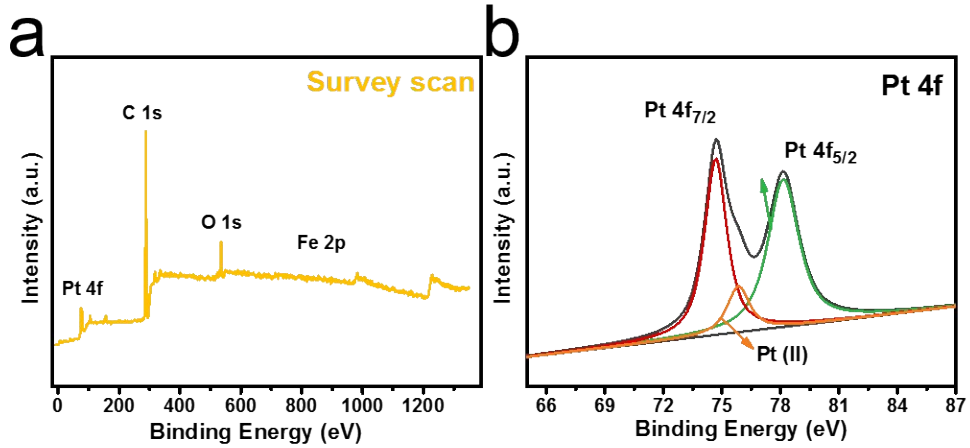

Fig. S7 XPS spectra of (a) survey scan, (b) Pt 4f in Pt_4Fe NWs.

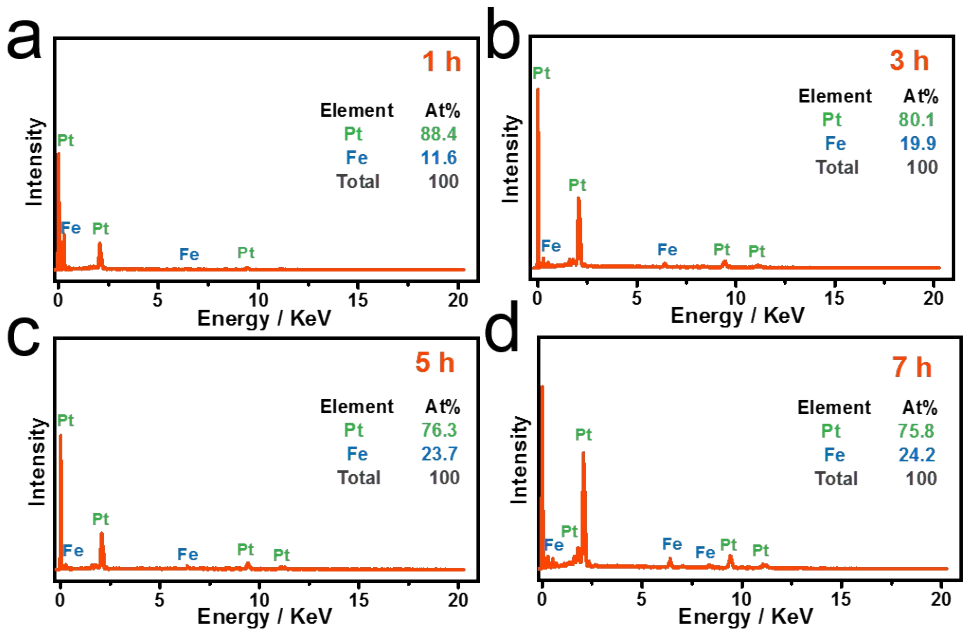

Fig. S8 SEM-EDS spectrum of Pt_3Fe NWs intermediates obtained after the reaction have been processed for (a) 1 h, (b) 3 h, (c) 5 h, and (d) 7h while keeping other conditions same.

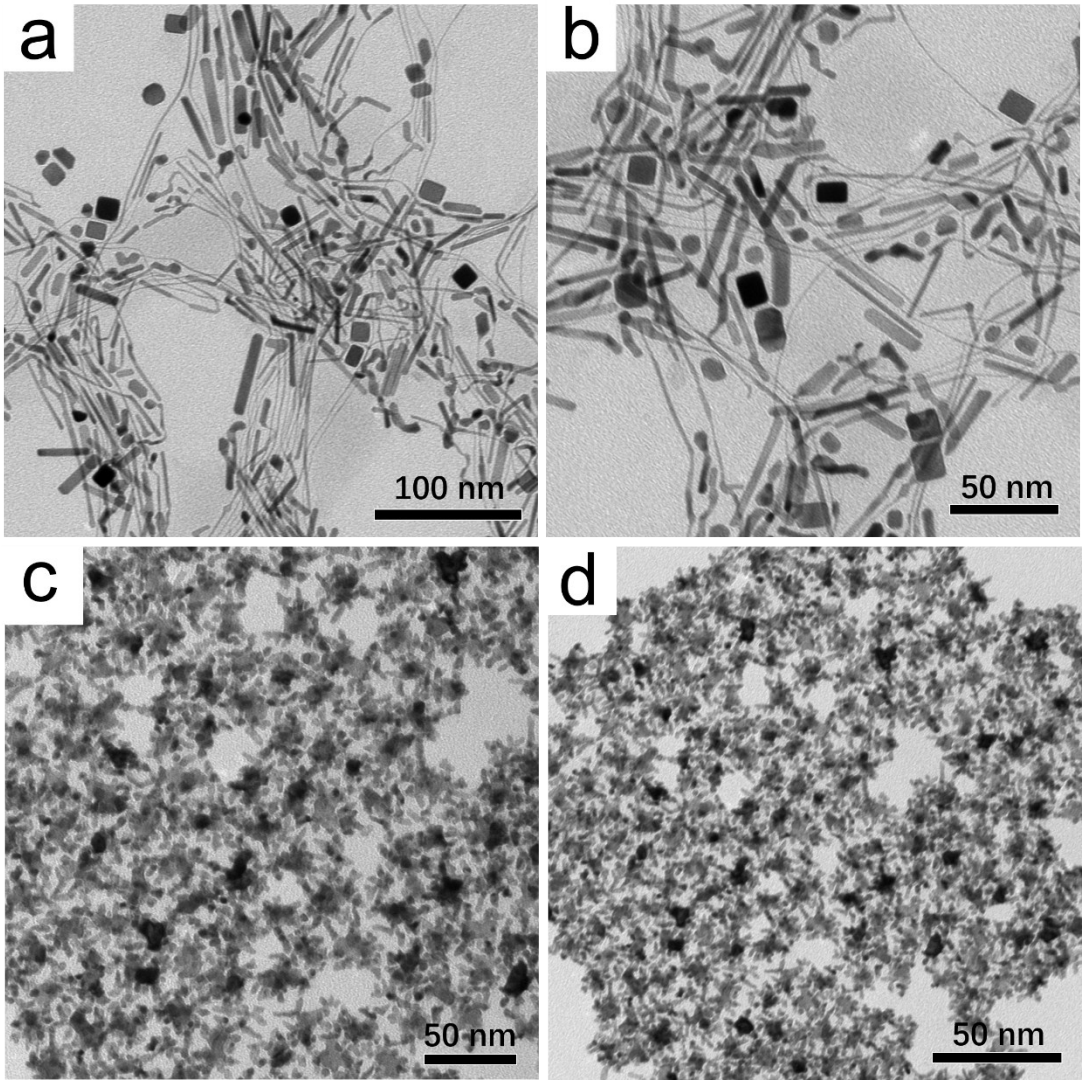

Fig. S9 TEM images of the products with the same reaction conditions as that of Pt_3Fe NWs without the addition of (a and b) $Fe(Ac)_2$, (c and d) CTAC.

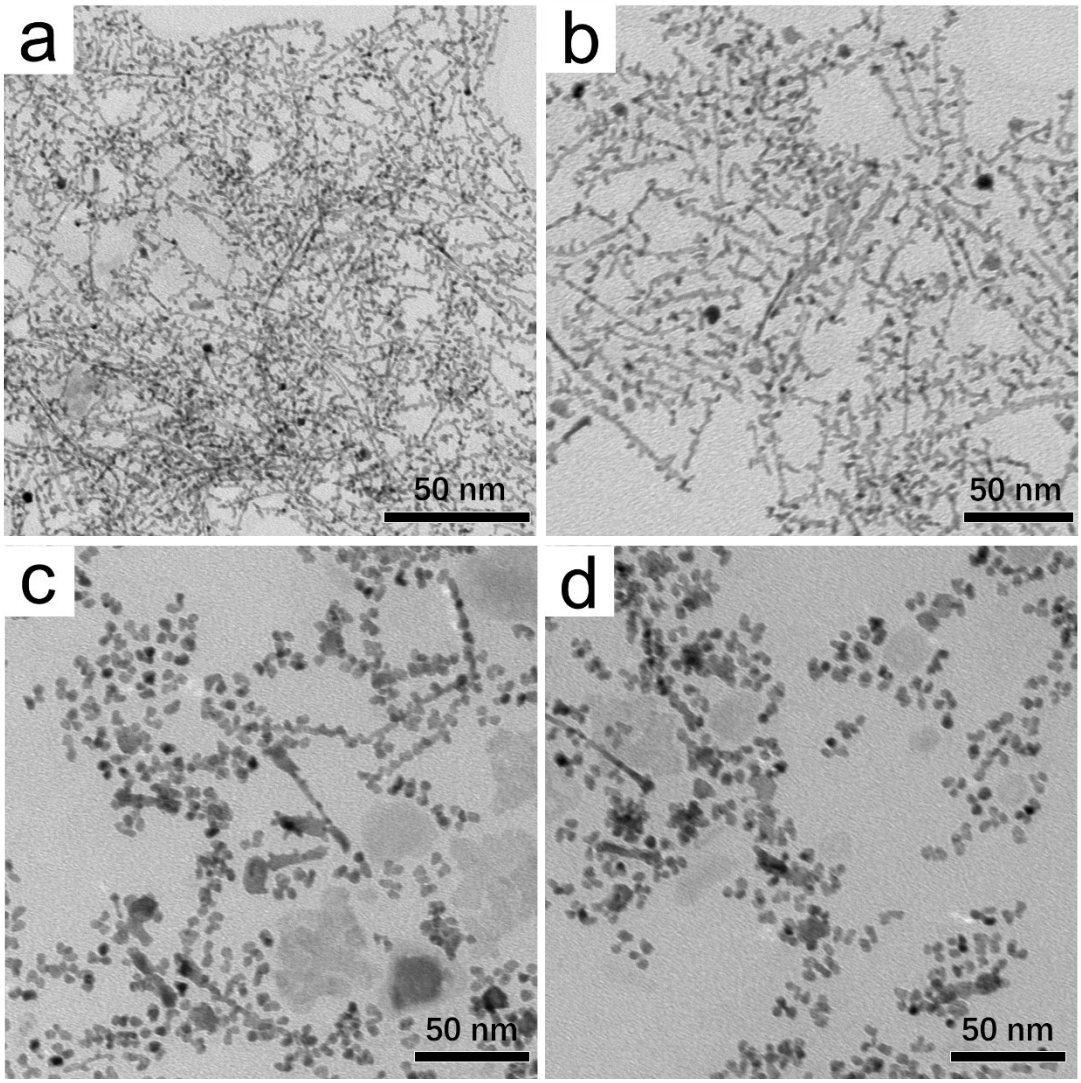

Fig. S10 TEM images of the products with the same reaction conditions as that of Pt_3Fe NWs without the addition of (a and b) phloroglucinol, (c and d) $W(CO)_6$.

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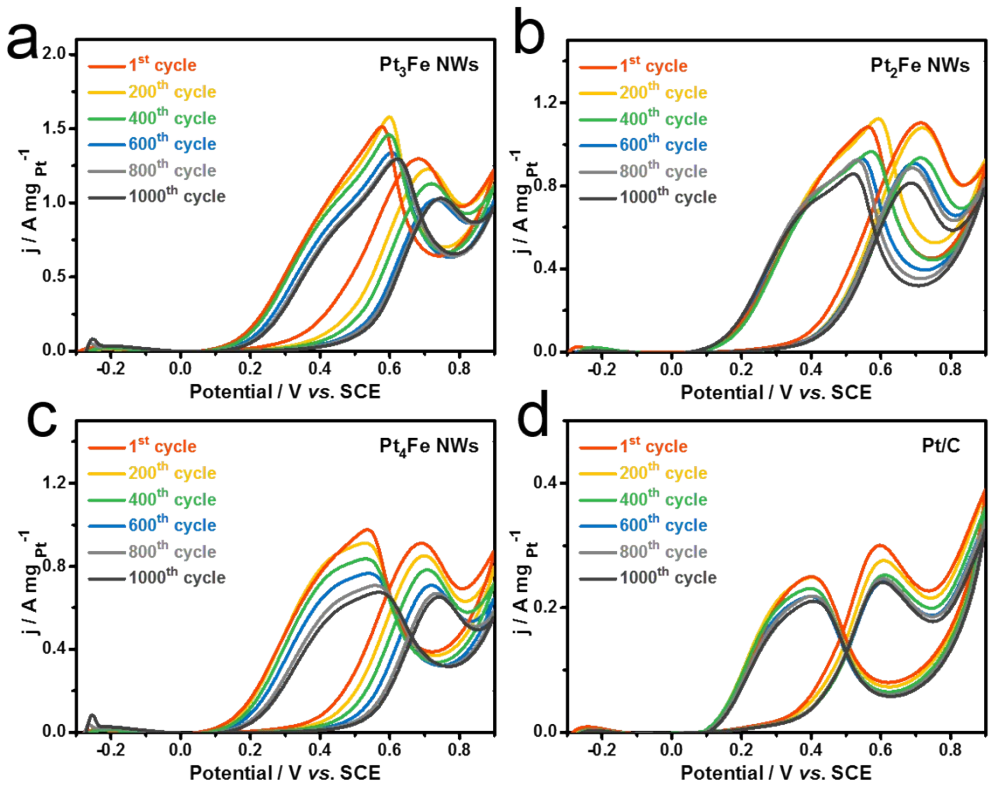

Fig. S11 CV (1st, 200th, 400th, 600th, 800th and 1000th) curves of (a) Pt_3Fe NWs, (b) Pt_2Fe NWs, (c) Pt_4Fe NWs, (d) Pt/C catalysts recorded in 0.1 M $HClO_4$ + 0.5 M ethanol solution.

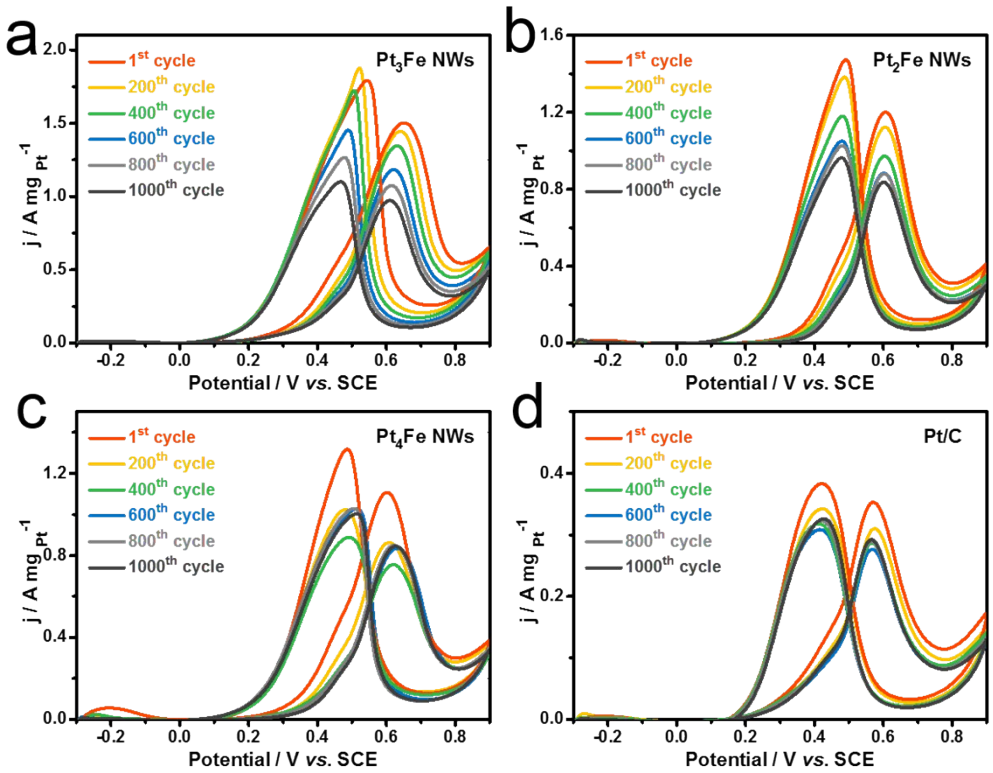

Fig. S12 CV (1st, 200th, 400th, 600th, 800th and 1000th) curves of (a) Pt_3Fe NWs, (b) Pt_2Fe NWs, (c) Pt_4Fe NWs, (d) Pt/C catalysts recorded in 0.1 M $HClO_4$ + 0.5 M methanol solution.

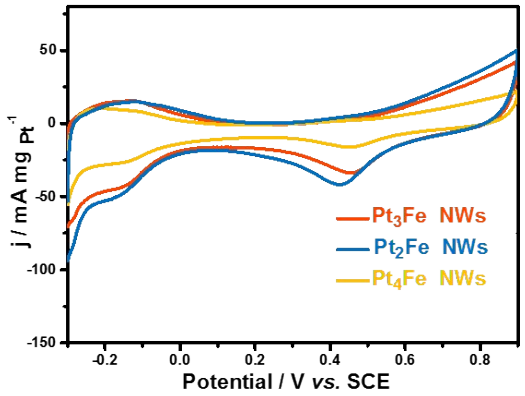

Fig. S13 CV curves of Pt_3Fe NWs, Pt_2Fe NWs, and Pt_4Fe NWs catalysts recorded in 0.1 M $HClO_4$ solution after durability tests.

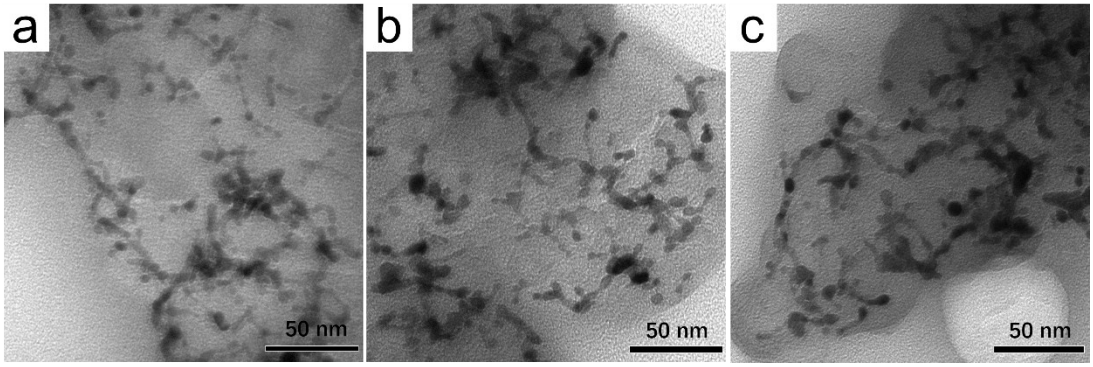

Fig. S14 The representative TEM images of (a) Pt_3Fe NWs, (b) Pt_2Fe NWs, (c) Pt_4Fe NWs after durability tests.

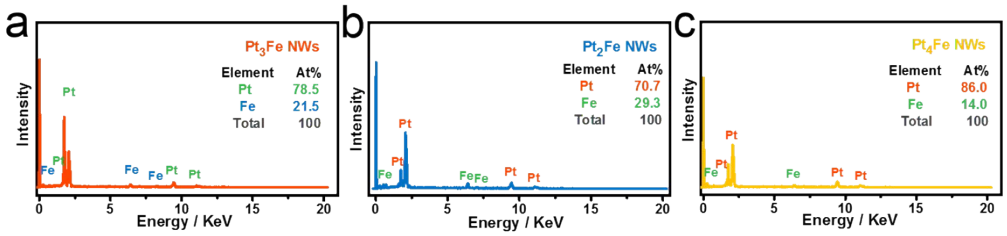

Fig. S15 SEM-EDS spectrum of (a) Pt_3Fe NWs, (b) Pt_2Fe NWs, (c) Pt_4Fe NWs catalysts after electrochemical durability test.

Table S1. EOR performances of Pt_3Fe NWs and various electrocatalysts from published works.

Catalysts	Peak currents from CV curves		Electrolyte	Reference
	J_m (A mg^{-1})	J_s (mA cm^{-2})		
Pt_3Fe NWs	1.30	4.01	0.1 M $HClO_4$ + 0.5 M Ethanol	This work
Pt-Cu Nanocone	~ 0.4	2.97	0.5 M H_2SO_4 + 0.1 M Ethanol	*J. Am. Chem. Soc.* **2013**, 135, 18304-18307.
THH PtNi NFs	0.77	1.99	0.5 M H_2SO_4 + 0.1 M Ethanol	*Nano Lett.* **2016**, 16, 2762-2767.
RDH PtNi NFs	0.98	1.79		
PtRhNi/C	0.378		0.5 M $HClO_4$ + 1 M Ethanol	*ChemElectroChem* **2015**, 2, 903-908
$PtPb_{0.27}$ NWs	~ 1.7	~ 0.9	0.1 M $HClO_4$ + 0.15 M Ethanol	*Chem. Mater.* **2016**, 28, 4447-4452.
$PtCu_{2.1}$ NWs	1.015	2.16	0.1 M $HClO_4$+ 0.2 M Ethanol	*Nano Lett.* **2016**, 16, 5037−5043
RuNi@PtRu/ SWCNT	0.9534		0.5 M H_2SO_4+ 1 M Ethanol	*Energy Environ. Sci.* **2011**, 4, 4513-4516.
PtRh NW/GNS	1	2.8	1 M H_2SO_4 + 1 M Ethanol	*ACS Appl. Mater. Interface* **2017**, 9, 3535-3543

Table S2. MOR performances of Pt_3Fe NWs and various electrocatalysts from published works.

Catalysts	Peak currents from CV curves		Electrolyte	Reference
	J_m (A mg^{-1})	J_s (mA cm^{-2})		
Pt_3Fe NWs	1.50	4.65	0.1 M $HClO_4$ + 1 M methanol	This work
Pt_3Cu Nanoicosahedra	0.736	2.14	0.1 M $HClO_4$ + 0.2 M methanol	*ACS Nano*, **2015**, 9, 7634-7640
Pt_3Cu Nanoctahedra	0.518	1.63		
PtFe NWs		1.20	0.5 M H_2SO_4 + 1 M Methanol	*Chem. Eur. J.* **2013**, 19, 233-239.
PtNi Concave Nanoctahedra	0.44	1.55	0.1 M $HClO_4$ and 1 M Methanol	*Angew. Chem. Int. Ed.* **2012**, 51, 12524-12528.
$Fe_{28}Pt_{38}Pd_{34}$ NWs	0.4887		0.1M $HClO_4$+ 0.2 M Methanol	*J. Am. Chem. Soc.* **2012**, 51, 15354-15357.
Pt_7Ru_2Fe NWs		2.27	0.1 M $HClO_4$ + 0.5 M Methanol	*Energy Environ. Sci.* **2015,** 8, 350-363.
PtPb CNCs	0.97	2.09	0.1 M $HClO_4$ +0.5 M Methanol	*Chem. Mater.* **2017**, 29, 4557-4562