

## Supporting Information

### Superior Electrocatalytic Activity from Nanodendritic Structure

### Consisting of a PtFe Bimetallic Core and Pt Shell

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### Experimental

#### Materials

The chloroplatinic acid hydrate and the 5 wt% Nafion solution were from the Aldrich Chemical Co. Commercial state-of-the-art Pt black (Aldrich Chemical Co.) was used as the benchmark for comparison. Ferrous gluconate, NaBH<sub>4</sub>, gluconic acid, and ferrous chloride hydrate were all obtained from Beijing Chemical Reagent Company (Beijing, China). Ultrapure water (Millipore, 18.2 MΩ cm) was used throughout all experiments.

#### Synthesis of PtFe@Pt nanodendrites

The PtFe@Pt nanodendrites with adjustable Pt/Fe atomic ratios were synthesized by co-reduction of the chloroplatinic acid hydrate and ferrous gluconate with NaBH<sub>4</sub> in aqueous solution. For a typical synthesis of PtFe@Pt nanodendrites with Pt/Fe atomic ratio of 3/1, an aqueous solution that containing 0.3 mM chloroplatinic acid hydrate and 0.1 mM ferrous gluconate were added into an 100 mL three-neck, round-bottomed flask, and the total volume was adjusted to 50 mL. Then the mixture was stirred under argon for 1 h to remove the oxygen. Subsequently, 5 mL aqueous solution containing 1.2 mM NaBH<sub>4</sub> was quickly injected into the flask. After stirring

for 5 min, the black nanocrystal dispersions were centrifuged washed several times with ethanol. All the procedure was conducted under ambient temperature. For comparison, PtFe nanocrystals with Pt/Fe atomic ratio of 3/1 were prepared using the similar method unless the precursor of Fe was the mixture of gluconic acid and ferrous chloride hydrate instead of ferrous gluconate.

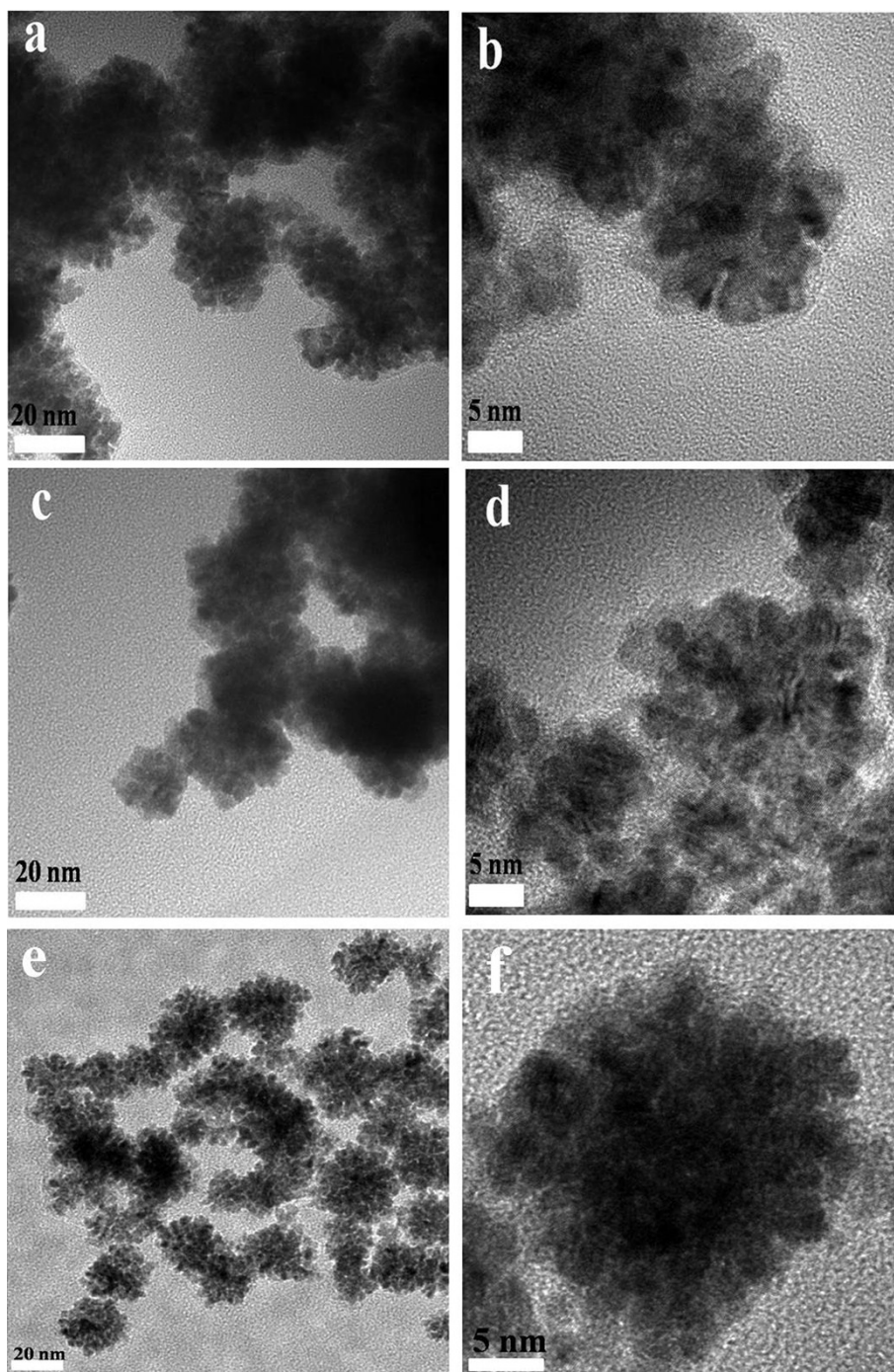
### **Physical characterizations**

Scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and element mapping analysis were conducted on a XL30 ESEM FEG field emission scanning electron microscope operating at 20 kV. Transmission electron microscopy (TEM) was used to analyze the size and morphology of catalysts on a Philips TECNAI G2 operating at 200KV. The X-ray diffraction (XRD) patterns of the catalysts were obtained using a PW1700 diffractometer (Philips Co.) with a Cu K $\alpha$  ( $\lambda = 0.15405$  nm) radiation source operating at 40 kV and 30 Ma. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos XSAM-800 spectrometer with an Mg K $\alpha$  radiation source. The bulk composition of catalyst was evaluated by both inductively coupled plasma optical emission spectrometer (X Series 2, Thermo Scientific USA).

### **Electrochemical measurements**

All electrochemical measurements were carried out with an EG&G mode 273 potentiostat/Galvanostat and a conventional three-electrode test cell at the ambient temperature. A glassy carbon disk coated with catalyst was used as the working electrode. The counter-electrode and reference-electrode were a Pt foil and a saturated

calomel electrode (SCE) respectively. The glassy carbon disk was polished with 0.3  $\mu\text{m}$  and 0.05  $\mu\text{m}$  alumina powder respectively, sonication and rinsed with deionized water before used. The homogeneous catalyst ink was prepared by ultrasonically dispersing the mixture of 5 mg catalyst, 950  $\mu\text{L}$  ethanol, and 50  $\mu\text{L}$  Nafion alcohol solution (Aldrich, 5 wt% Nafion) for approximately 30 min. Next, 5 $\mu\text{L}$  catalyst ink was pipetted and spread on a 3 mm-diameter pre-cleaned glassy carbon disk as the working electrode. All electrolyte solutions were deaerated by high-purity nitrogen for at least 15 min prior to any measurement. All of the potentials are relative to the SCE electrode, unless otherwise noted. To activate and clean the catalyst surface, the working electrodes were potentially scanned from -0.2 V and 0.958 V vs. SCE at a scan rate of 50  $\text{mV s}^{-1}$  in a 0.5 M  $\text{H}_2\text{SO}_4$  solution until a stable response was obtained. For CO stripping voltammetric experiments, CO was absorbed at 0.02 V vs. SCE in 0.5 M  $\text{H}_2\text{SO}_4$  solution for 10 min, excess CO in the electrolyte was then purged out with  $\text{N}_2$  for 10 min, and then two first cycles recorded at 20  $\text{mV s}^{-1}$ . To evaluate the catalytic activity for methanol, the cyclic voltammetry experiments were carried out in 0.5 M  $\text{H}_2\text{SO}_4$  + 1 M  $\text{CH}_3\text{OH}$  solution with a scan rate of 50  $\text{mVs}^{-1}$ . The chronoamperometry experiments were performed in the same solution at the potential of 0.5V (vs. SCE) for 3600 s. Accelerated durability tests were conducted in 0.5 M  $\text{H}_2\text{SO}_4$  + 1 M  $\text{CH}_3\text{OH}$  solution with a scan rate of 50  $\text{mVs}^{-1}$  and the scan range was -0.2 – 0.958 V (vs. SCE).



**Fig S1** TEM images of PtFe nanodendrites with different Pt/Fe ratios: (a, b) Pt/Fe=1:1, (c, d) Pt/Fe=2:1 (e, f) Pt/Fe=4:1.

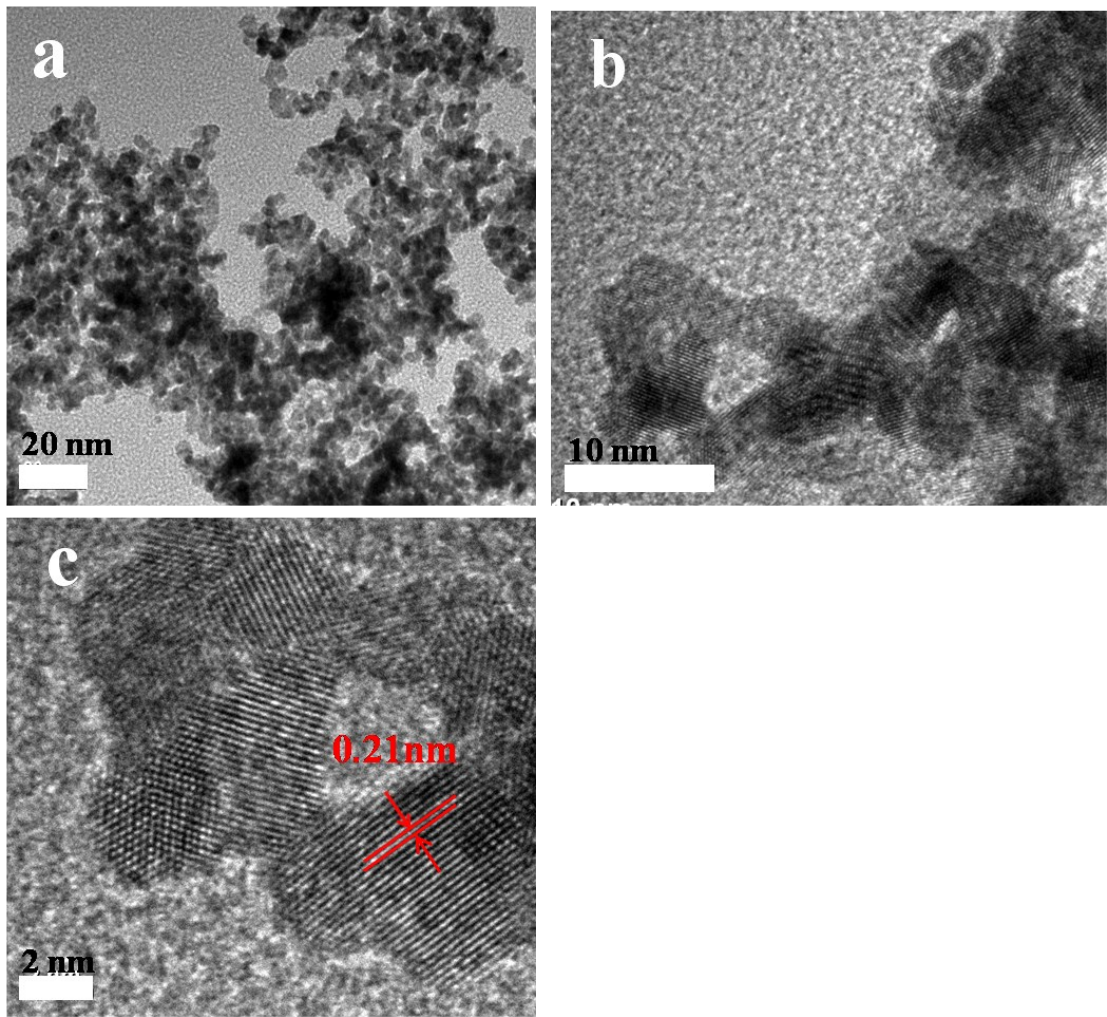
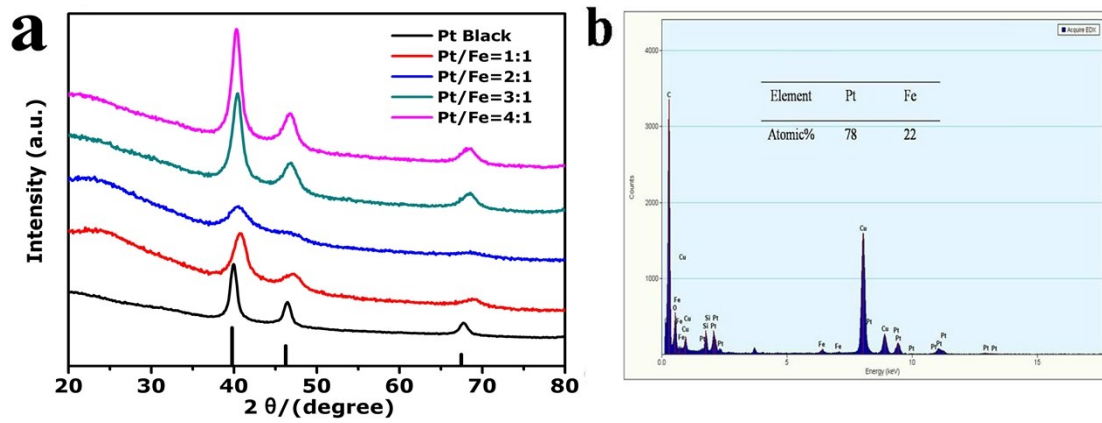
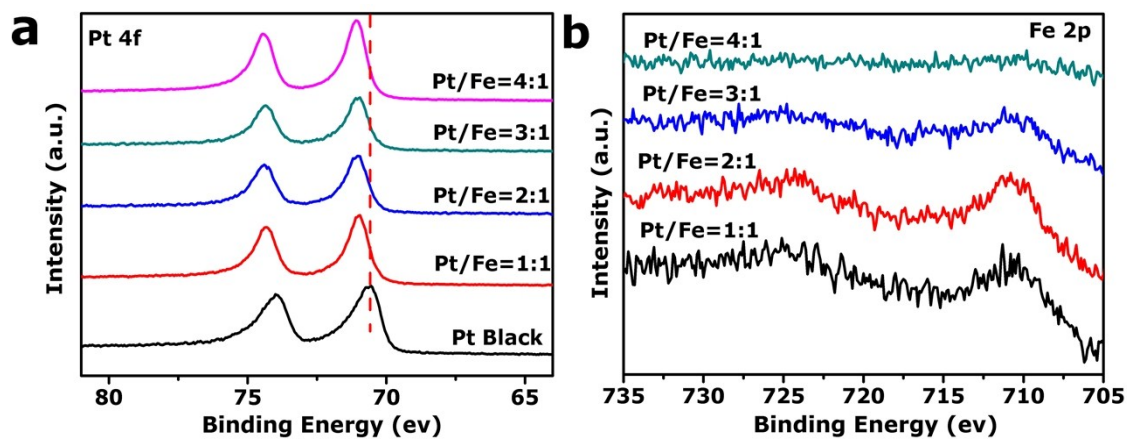


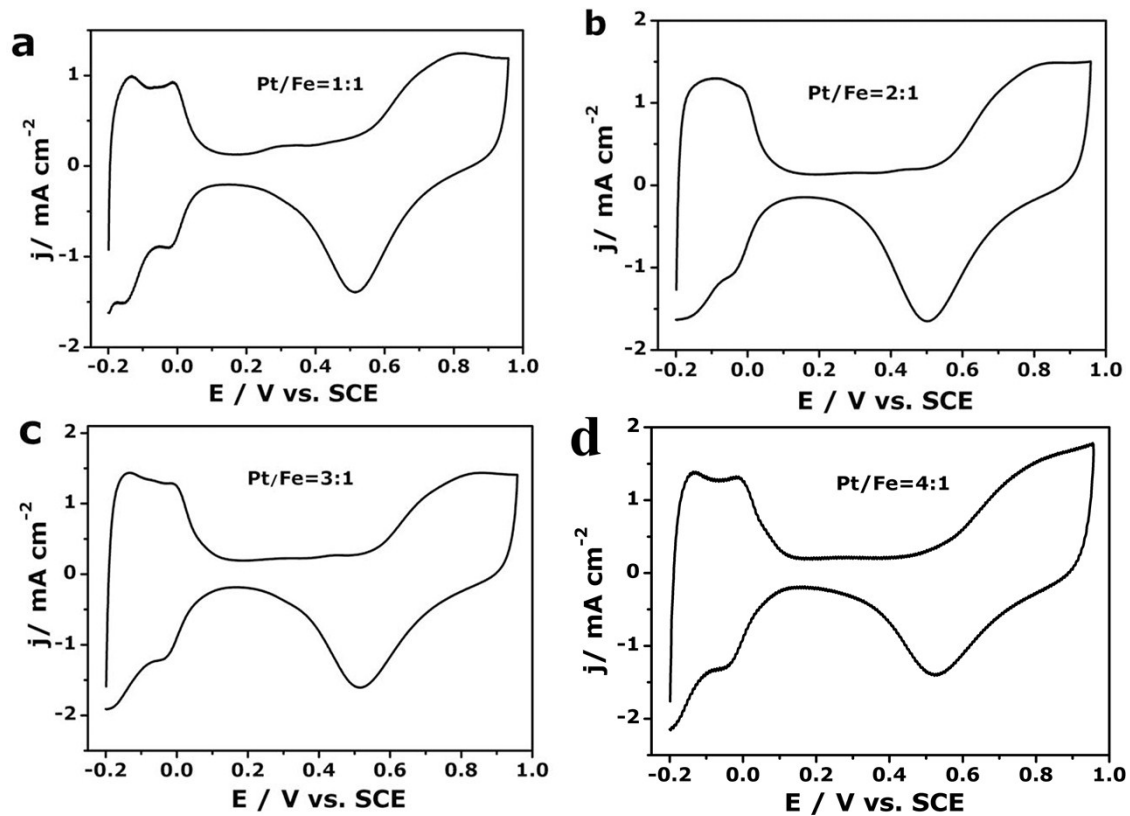
Fig S2 TEM images of sample prepared with gluconic acid and ferrous chloride as precursor.



**Fig S3** XRD patterns of the PtFe nanodendrite catalysts with different Pt/Fe ratios (a) and EDX analysis of PtFe@Pt catalyst (b).

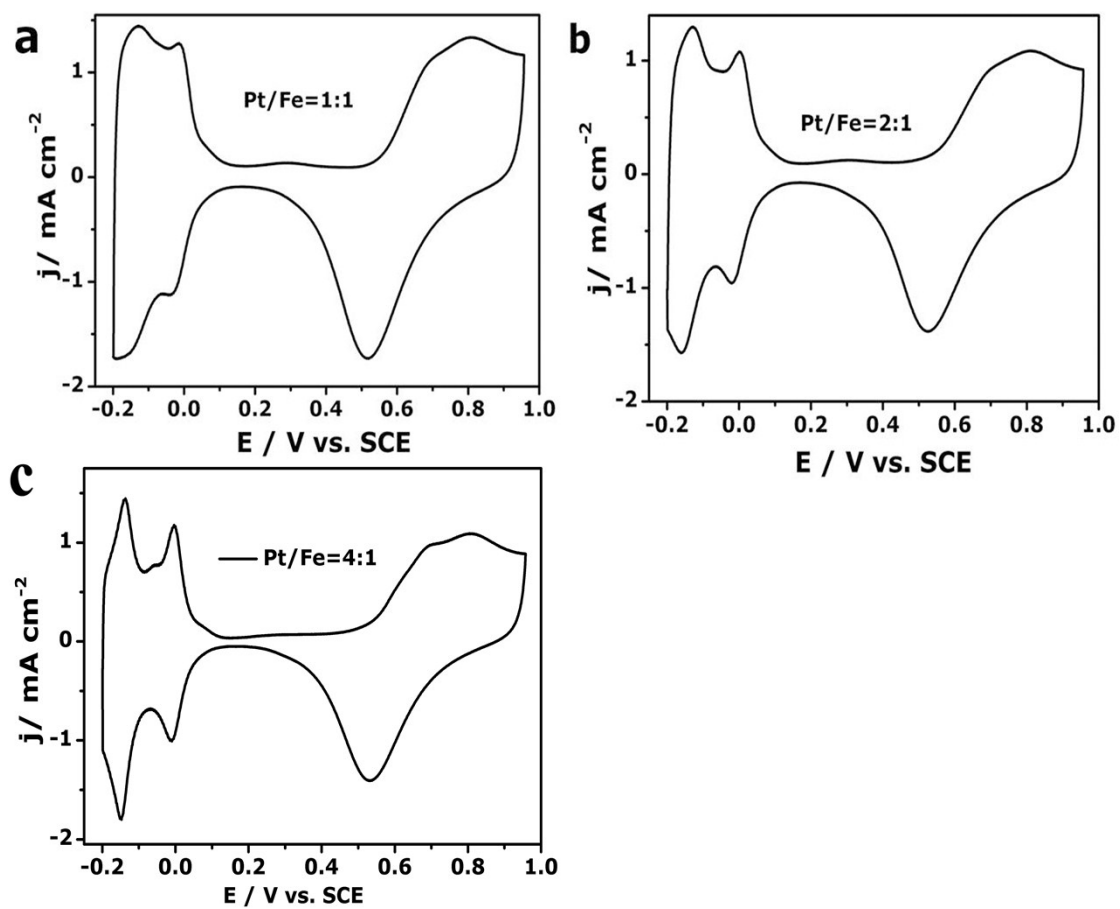


**Fig S4** (a) Pt 4f and (b) Fe 2p XPS spectra of the synthesized PtFe@Pt catalysts with different Pt/Fe ratios.

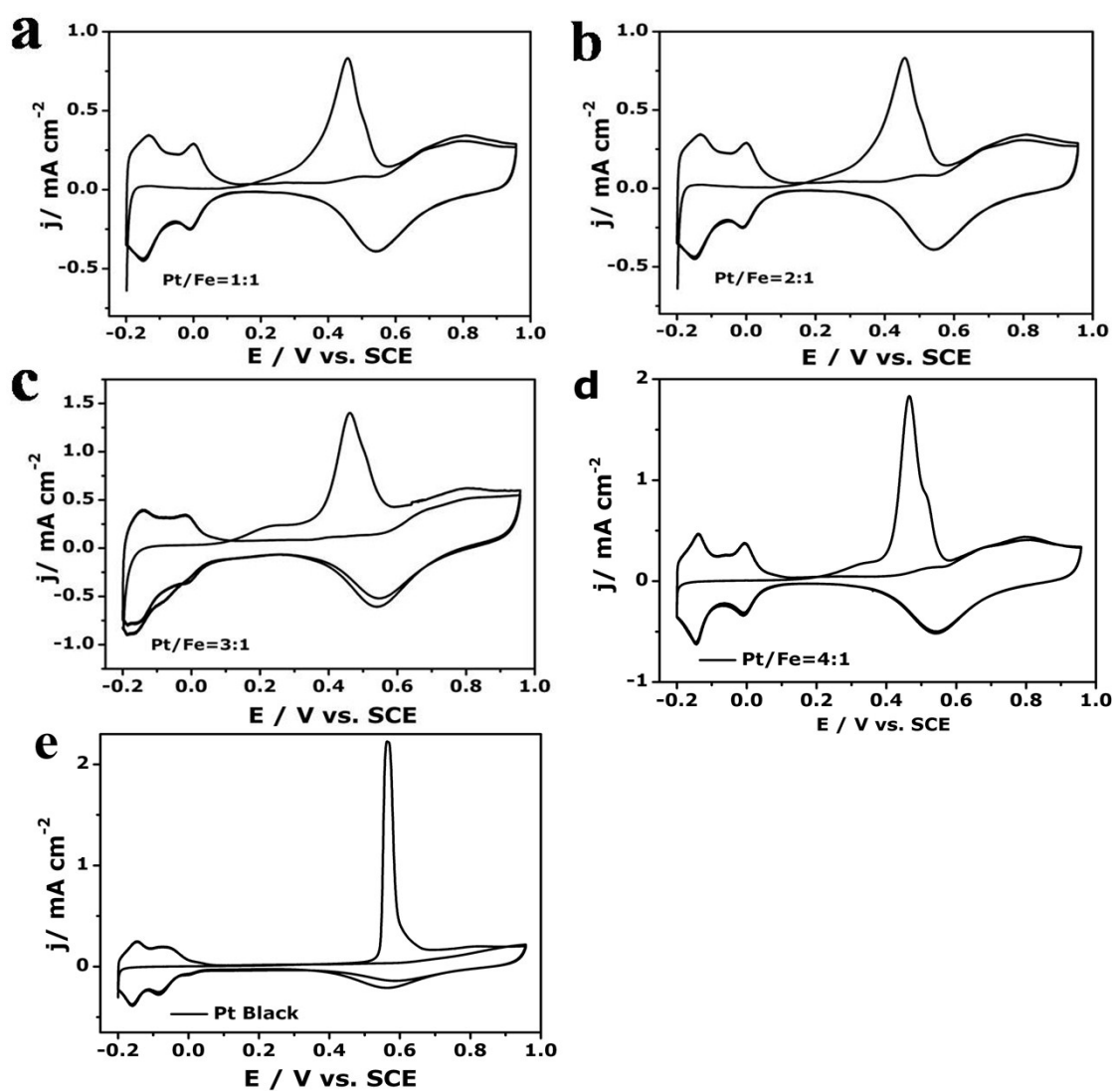


**Fig S5** The initial cyclic voltammograms of Pt/Fe nanodendrites catalysts with different Pt/Fe ratios in N<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, (a) Pt/Fe=1:1, (b) Pt/Fe=2:1, (c) Pt/Fe=3:1, (d) Pt/Fe=4:1.

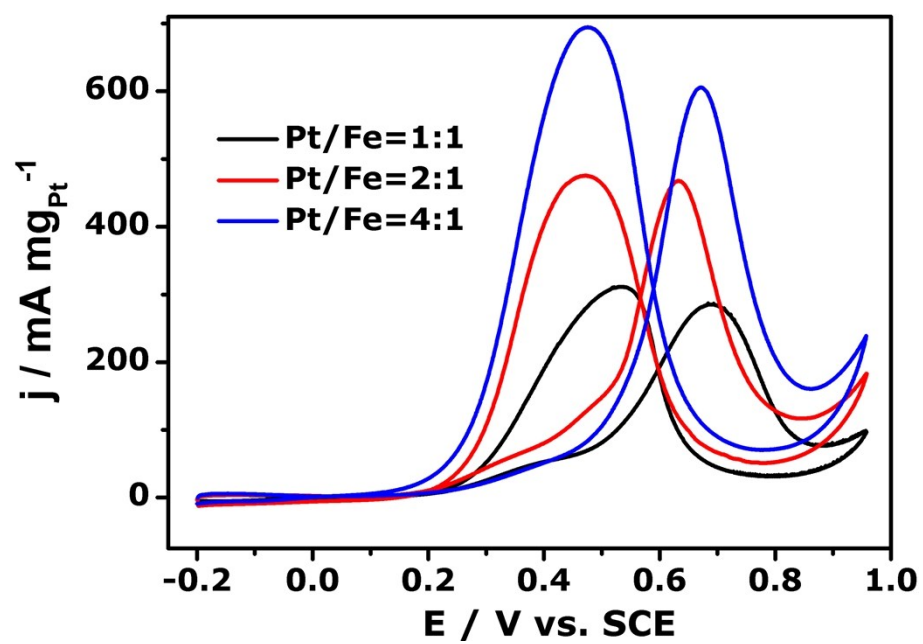




**Fig S6** The stable Cyclic voltammograms of PtFe nanodendrites in N<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with different Pt/Fe ratios: (a) Pt/Fe=1:1, (b) Pt/Fe=2:1, (c) Pt/Fe=4:1.



**Fig S7** CO stripping voltammograms of the PtFe@Pt and commercial Pt black catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at a sweep rate of 20 mVs<sup>-1</sup>; (a) Pt/Fe=1:1, (b) Pt/Fe=2:1, (c) Pt/Fe=3:1, (d) Pt/Fe=4:1 and (e) Pt black.



**Fig S8** Cyclic voltammograms of PtFe@Pt with different Pt/Fe ratio in 0.5 M  $\text{H}_2\text{SO}_4$  + M  $\text{CH}_3\text{OH}$  at room temperature with sweep rate of  $50 \text{ mV s}^{-1}$ .

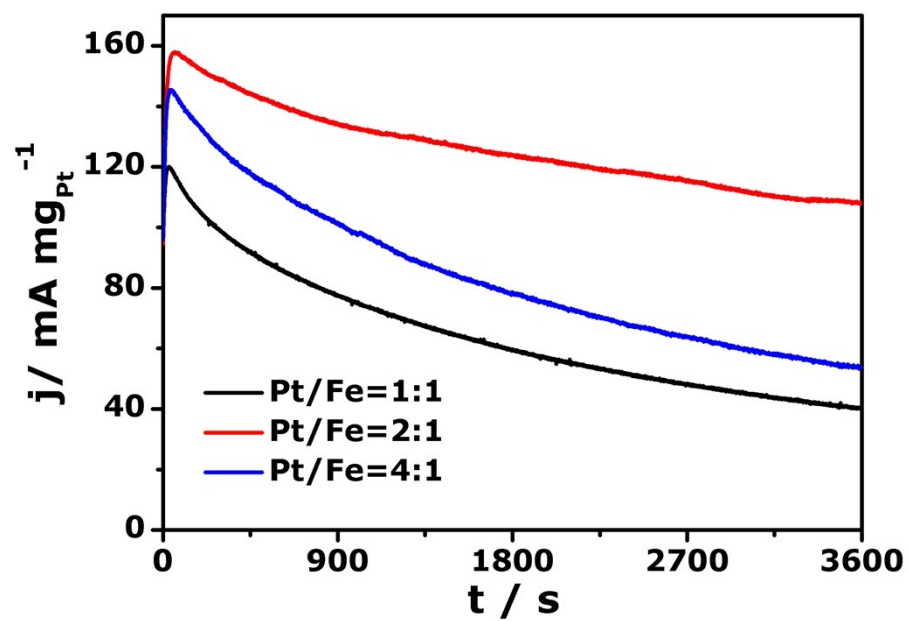
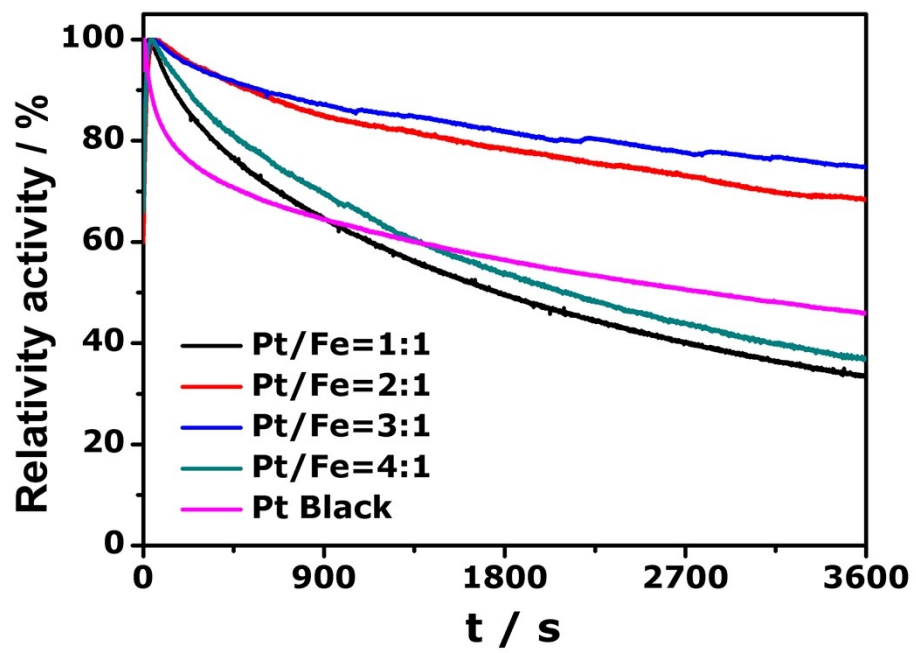
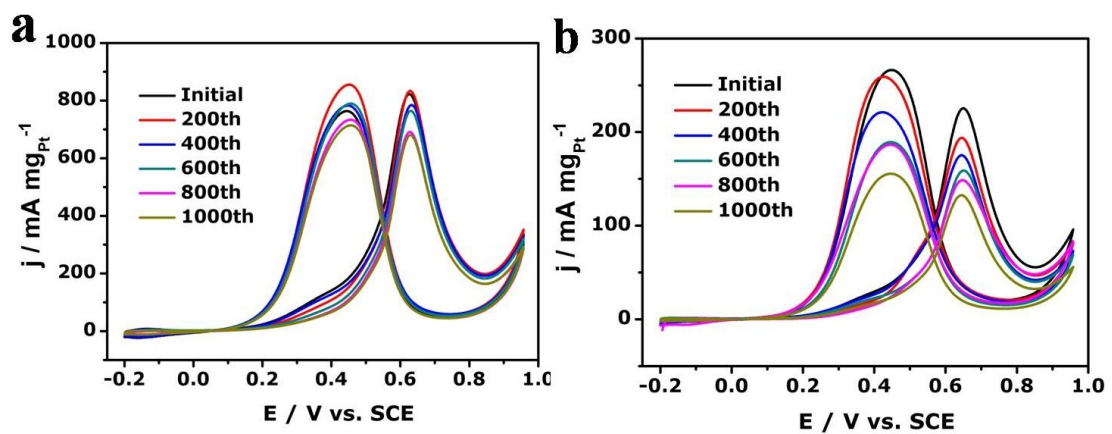


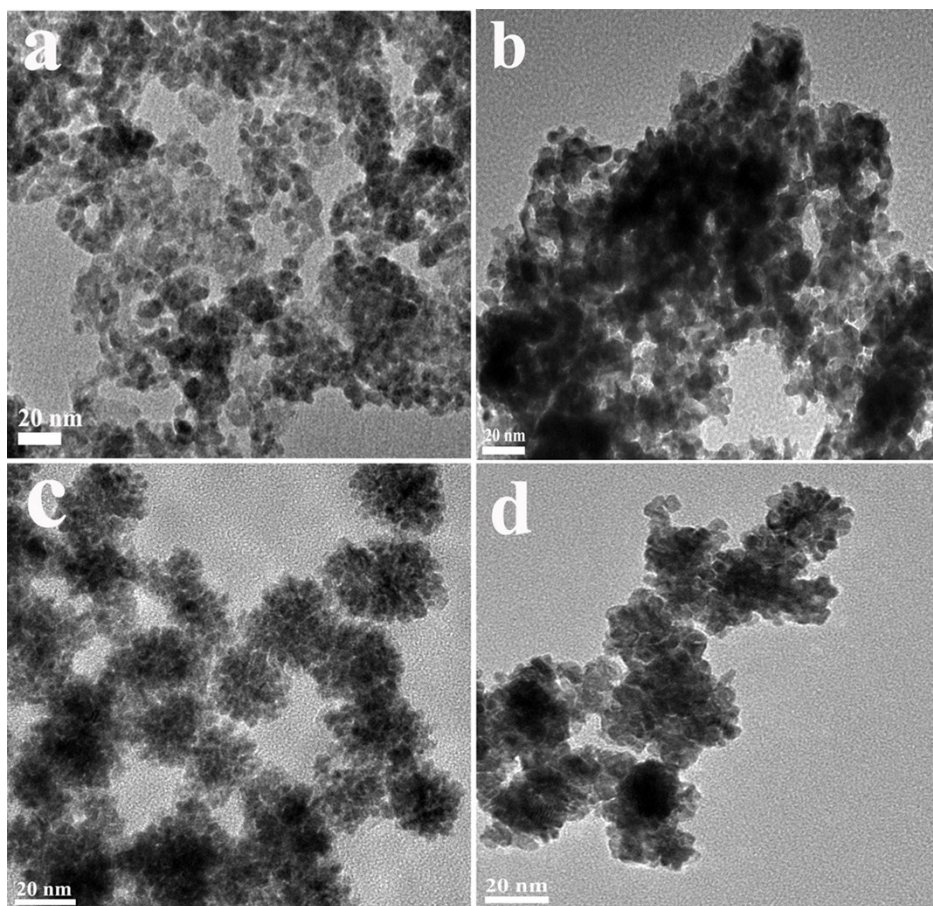
Fig S9 Chronoamperometric results for PtFe with different Pt/Fe ratio in 0.5 M  $\text{H}_2\text{SO}_4$  + M  $\text{CH}_3\text{OH}$  at room temperature.



**Fig S10** Relative activity of PtFe with different Pt/Fe ratio in 0.5 M H<sub>2</sub>SO<sub>4</sub> + M CH<sub>3</sub>OH at room temperature during chronoamperometric test.



**Fig S11** Cyclic voltammograms in 1 M CH<sub>3</sub>OH + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution for (a) PtFe@Pt, (b) Pt black during the APCT.



**Fig. S12** TEM images of Pt black and PtFe@Pt catalyst before and after 1000 cycles, (a) Pt black before 1000 cycles; (b) Pt black after 1000 cycles; (c) PtFe@Pt before 1000 cycles; (d) PtFe@Pt after 1000 cycles.

**Table S1 Element contents of the PtFe@Pt catalysts**

<b>Sample</b>	<b>XPS / at%</b>		<b>ICP-OES / at%</b>	
	<b>Fe</b>	<b>Pt</b>	<b>Fe</b>	<b>Pt</b>
<b>Pt/Fe=1: 1</b>	<b>7.28</b>	<b>92.72</b>	<b>48.04</b>	<b>51.96</b>
<b>Pt/Fe=2: 1</b>	<b>6.97</b>	<b>93.03</b>	<b>31.64</b>	<b>68.36</b>
<b>Pt/Fe=3: 1</b>	<b>6.33</b>	<b>93.67</b>	<b>23.07</b>	<b>76.93</b>
<b>Pt/Fe=4: 1</b>	<b>4.86</b>	<b>95.14</b>	<b>23.91</b>	<b>76.09</b>



**Table S2 Electrochemical performance of the catalysts**

	CO Stripping/mV				MOR activity	
	Peak potential	Onset potential	$\Delta E_{\text{Peak}}$	$\text{ECSA}_{\text{CO}}/\text{m}^2/\text{g}$	Mass activity / $\text{mA mg}_{\text{Pt}}$	Specific activity / $\text{mA cm}^{-2}$
<b>Pt/Fe=1: 1</b>	<b>455</b>	<b>168</b>	<b>-110</b>	<b>10.08</b>	<b>286.5</b>	<b>2.84</b>
<b>Pt/Fe=2: 1</b>	<b>460</b>	<b>239</b>	<b>-105</b>	<b>14.89</b>	<b>463.3</b>	<b>3.11</b>
<b>Pt/Fe=3: 1</b>	<b>462</b>	<b>111</b>	<b>-103</b>	<b>21.54</b>	<b>821.1</b>	<b>3.81</b>
<b>Pt/Fe=4: 1</b>	<b>467</b>	<b>207</b>	<b>-98</b>	<b>22.37</b>	<b>605.5</b>	<b>2.71</b>
<b>Pt Black</b>	<b>565</b>	<b>498</b>	<b>-</b>	<b>11.97</b>	<b>224.1</b>	<b>1.87</b>