N-doped carbon confined CoFe@Pt nanoparticles with robust catalytic performance for methanol oxidation reaction

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Table of Contents

Experimental section

Fig. S1 TEM of CFNPs-PDA-x0.5 at different magnifications.

Fig. S2 FTIR of CFNPs, CFNPs-PDA-x0.5, CoFe@Pt-NCs-x0.5-T700-t360.

Fig. S3 XRD of CFNPs, CFNPs-PDA-x0.5, CoFe-NCs-x0.5-T700.

Fig. S4 Raman of CoFe@Pt-NCs-x0.5-T700-t360.

Table S1. Elements wt% in catalysts obtained from ICP-OES measurement.

Fig. S5 XPS of Pt/C, CoFe-NCs-x0.5-T700, CoFe@Pt-NCs-x0.5-T700-t360.

Fig. S6 Comparing element contents by the results of ICP-OES and XPS for CoFe@Pt-NCs-x0.5-T700-t360.

Fig. S7 CV curves of CoFe@Pt-NCs-x0.5-T700-t360 and Pt/C normalized by ECSA in 0.5 M H_2SO_4 at different scan rates.

Fig. S8 CV curves of CoFe-NCs-x0.5-T700 in 0.5 M H_2SO_4 + 0.5 M CH₃OH at the scan rate of 50 mV·s⁻¹.

Fig. S9 TEM of (a) CoFe@Pt-NCs-x0.1-T700-t360, (b) CoFe@Pt-NCs-x0.3-T700-t360, (c) CoFe@Pt-NCs-x0.7-T700-t360, (d) CoFe@Pt-NCs-x1.0-T700-t360.

Fig. S10 CV curves of CoFe@Pt-NCs-x0.1-T700-t360 (a=0.1, 0.3, 0.7, 1.0) in 0.5 M H_2SO_4 at the scan rate of 50 mV·s⁻¹.

Fig. S11 CV curves of CoFe@Pt-NCs-xa-T700-t360 (a=0.1 (a), 0.3 (b), 0.7 (c), 1.0
(d)) in 0.5 M H₂SO₄ + 0.5 M CH₃OH solution at different scan rates.

Fig. S12 CV curves of (a) CoFe@Pt-NCs-xa-T700-t360 (a=0.1, 0.3, 0.7, 1.0) and (b) CoFe@Pt-NCs-x0.5-Tb-tc normalized by ECSA in 0.5 M H_2SO_4 at the scan rate of 50

mV·s⁻¹.

Fig. S13 Raman of CoFe@Pt-NCs-xa-T700-t360 (a=0.1, 0.3, 0.7, 1).

Fig. S14 Temperature-programmed reduction curves of (a) CFNPs, (b) PDA, (c) CFNPs-PDA-x0.5.

Fig. S15 CV curves of CoFe@Pt-NCs-x0.5-Tb-tc in 0.5 M H₂SO₄.

Fig. S16 CV curves of CoFe@Pt-NCs-x0.5-Tb-tc (a) b=700, c=60; (b) b=700, c=20;

(c) b=700, c=0; (d) b=600, c=0; (e) b=500, c=0; in 0.5 M H₂SO₄ + 0.5 M CH₃OH solution

at different scan rates (scan rate: 75, 100, 125, 150, and 200 mV·s⁻¹).

Fig. S17 Deconvoluted XPS of Pt 4f for catalysts.

Fig. S18 Deconvoluted XPS of Co 2p for catalysts.

Fig. S19 Deconvoluted XPS of Fe 2p for catalysts.

Fig. S20 Deconvoluted XPS of N 1s for catalysts.

Fig. S21 Atomic concentration of Co 2p tested by XPS for CoFe@Pt-NCs-x0.5-Tb-

tc (a) b=500, c=0; (b) b=600, c=0; (c) b=700, c=0.

Fig. S22 Temperature-programmed curves of CFNPs-PDA-x0.5.

Fig. S23 Temperature-programmed curves of CFNPs-PDA-x0.5; (a) temperature

setting routine, (b) temperature programmed decomposition and reduction.

Fig. S24 XRD of CFNPs-PDA-x0.5 after temperature-programmed decomposition and reduction.

Fig. S25 TG/DTA of CFNPs-PDA-x0.5 after temperature-programmed

decomposition and reduction; (a) Ar, (b) Air.

Fig. S26 EIS of catalysts.

Fig. S27 CV curves (a) CoFe@Pt-NCs-x0.5-T700-t0 and (b) Pt/C in 0.5 M H_2SO_4 +

 $0.5 \text{ M CH}_3\text{OH}$ for 1000 Cycles. (c) Mass activity during 1000 cycles.

Fig. S28 CO stripping patterns recorded on CoFe@Pt-NCs-x0.5-T700-t0.

Table S2. Comparison of methanol oxidation behavior on the CoFe@Pt-NCs-

X0.5-T700-t0 composite and various Pt-based electrocatalysts

Experimental section

Reagents and chemicals

Chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$), dopamine, aminomethane (tris), CH₃OH, Carbon black (Vulcan XC-72), H_2SO_4 , DMF were all purchased from Macklin. Nafion (5 wt%) solution was purchased from alfa aesar. Pt/C-JM (20 wt%) was obtained from Johnson Matthey Company. All chemicals were of high-purity analytical grade. Besides, the CoFe₂O₄ nanoparticles (CFNPs) were obtained according to a previously reported method¹.

Preparation of CoFe@Pt-NCs

CoFe@Pt-NCs were prepared by applying a solution polymerization, pyrolysis, and galvanic replacement reaction with CFNPs as the precursor. During a typical synthesis procedure, 100 mg CFNPs, 121.1 mg tris and 50 mg dopamine were ultrasonically dispersed in 100 g of water. The obtained suspension was then stirred at room temperature. When the reaction was completed, the dispersion was collected and further purified by water three times. After drying in a vacuum dryer, the CFNPs-Pda-x0.5 was prepared. Then, 80 mg of CFNPs-PDA-x0.5 was calcined at 700 °C for 2 h in a 5% H₂/95% Ar atmosphere to prepare CoFe-NCs-x0.5-T700. Finally, CoFe-NCs-x0.5-T700 and H₂PtCl₆·6H₂O were added to 11.00 g DMF, whereas after were ultrasonically reacted for 10 min, the suspension was stirred at 60 °C for 360 min. The finally obtained dispersion was separated and washed with water. Subsequently, it was dried at 60 °C for 3 h, and finally, the CoFe@Pt-NCs-x0.5-T700t360 was obtained. The symbol x0.5 represents that the mass ratio of dopamine to CFPNs is 0.5, T700 shows that the pyrolysis temperature is 700 °C, and T360 denotes the time of galvanic displacement reaction by stirring is 360 min.

To optimize the structure of the CoFe@Pt-NCs, the mass ratio of dopamine /CFNPs xa (a =0.1, 0.3, 0.5, 0.7, 1.0 g/g), the pyrolysis temperature Tb (b =500, 600 and 700 °C) and the time of galvanic replacement tc (c=0, 20, 60 and 360 min) were adjusted, respectively. Additionally, a series of CoFe@Pt-NCs-xa-Tb-tc were prepared by following the above procedure.

As a reference, NCs were prepared by enforcing a solution polymerization and pyrolysis procedure. After adding 0.1211 g tris and 1 g dopamine into a beaker containing 100 g water, the obtained solution was then stirred at room temperature for 8 h. After washing with water three times, polydopamine (PDA) was obtained. The NCs were obtained after pyrolysis of PDA in 5% $H_2/95\%$ Ar at 700 °C for 2 h.

Characterizations

A spectrum One FTIR analyzer manufactured by Perkin-Elmer was used to characterize the functional groups contained in the prepared samples. A JEM1200EX microscope was employed to acquire TEM images. On top of that, a Talos F200X analytical electron microscope was utilized to obtain High-resolution TEM (HR-TEM) images, and the corresponding energy-dispersive X-ray spectroscopy mapping images, elemental line, and the selected area electron diffraction (SAED) images. The composition and crystal type of the samples were analyzed by using a Ultima IV Xray polycrystalline powder diffractometer that was made by Neo Science Company, Japan with a Cu-Ka radiation source. The N₂ adsorption/desorption isotherms were carried out to analyze the surface area and the pore size distribution. A WCT-1D thermogravimetric/differential thermal analyzer (TG/DTA) and temperatureprogrammed reduction (TPR) were used to analyze the thermal reactivity of the samples. The heating procedure of the TPR is as follows. The catalyst was heated from room temperature to 100 °C by 10 °C /min; after heat preservation for 30 min at 100 °C, the temperature continues to rise to 700 °C by 10 °C /min, followed by natural cooling. And the thermal conductivity detector was applied to detect the change of atmospheric composition and output signals, which were used to determine the decomposition temperature and products.

Finally, an AXIS Ultra X-ray photoelectron spectrometer (Kratos, UK) was utilized to analyze the surface elemental composition and electronic structure of the elements.

Electrochemical measurements

Electrochemical tests were also carried out with a CHI760D electrochemical workstation. Along these lines, high purity nitrogen was pumped into the electrolyte for 20 minutes prior to all the electrochemical tests to remove oxygen from the solution. For the preparation of the catalyst ink, 2.0 mg of catalyst was mixed with 500 μ l ethanol, 490 μ l water, and 10 μ l Nafion solution by ultrasonic for 1 h.

Subsequently, 10 μ l of the prepared suspension was deposited on the surface of glassy carbon electrode (GCE). The MOR performance was evaluated in a N₂-saturated 0.5 M CH₃OH+0.5 M H₂SO₄ solution scanned from -0.24 V to 0.96 V (vs. SCE). A chronoamperometry test was also performed to determine the stability of the catalyst at 0.65 V vs. SCE for 3600 s. The current densities that were obtained by the chronoamperometric measurement at 0.1 s and 3600 s were abbreviated to j_{0.1} and j₃₆₀₀, respectively. The retention rate was calculated from (1).

Retention rate of current density (%) =
$$\frac{j_{3600}}{j_{0.1}} *100$$
 (1)

As far as the CO-stripping measurements are concerned, the catalyst-modified GCE was immersed within a 0.5 M H_2SO_4 solution for 30 min at -0.2 V. To ensure that the catalyst was fully poisoned by CO, the CO gas was bubbled into the solution for 30 min. Then, CO removed oxygen from the solution by pumping in Ar. Moreover, the CV curves were recorded (vs. SCE) at a scan rate of 100 mV·s⁻¹.



Fig. S1 TEM of CFNPs-PDA-x0.5 at different magnifications.



Fig. S2 FTIR of CFNPs, CFNPs-PDA-x0.5, CoFe@Pt-NCs-x0.5-T700-t360.



Fig. S3 XRD of CFNPs, CFNPs-PDA-x0.5, CoFe-NCs-x0.5-T700.



Fig. S4 Raman of CoFe@Pt-NCs-x0.5-T700-t360.

Table S1. Elements wt% in catalysts obtained from ICP-OES measurement

Samples	Co wt%	Fe wt%	Pt wt%	NCs wt%	Pt/Fe	Co/Fe	А
CoFe@Pt-NCs-X0.1-T700-t360	26.68	53.88	6.33	13.11	0.0336	0.4692	100.0
CoFe@Pt-NCs-X0.3-T700-t360	25.89	51.92	5.44	16.75	0.0300	0.4725	89.2
CoFe@Pt-NCs-X0.5-T700-t360	24.77	49.64	5.09	20.50	0.0294	0.4728	87.3
CoFe@Pt-NCs-X0.7-T700-t360	23.76	47.79	4.66	23.79	0.0279	0.4711	83.0
CoFe@Pt-NCs-X1.0-T700-t360	23.87	47.84	4.23	24.06	0.0253	0.4728	75.3
CoFe@Pt-NCs-X0.5-T700-t60	25.16	50.26	4.57	20.01	0.0260	0.4743	77.4
CoFe@Pt-NCs-X0.5-T700-t20	25.24	49.75	4.49	20.52	0.0258	0.4807	76.8
CoFe@Pt-NCs-X0.5-T700-t0	24.12	48.37	4.39	23.12	0.0260	0.4725	77.3
CoFe@Pt-NCs-X0.5-T600-t0	24.43	49.26	3.99	22.32	0.0232	0.4700	68.9
CoFe@Pt-NCs-X0.5-T500-t0	28.69	57.66	3.77	9.88	0.0187	0.4714	55.7

A is the relative value of Pt/Fe of CoFe@Pt-NCs (based on CoFe@Pt-NCs-x0.1-T700-t360).



Fig. S5 XPS of Pt/C, CoFe-NCs-x0.5-T700, CoFe@Pt-NCs-x0.5-T700-t360.



Fig. S6 Comparing element contents by the results of ICP-OES and XPS for CoFe@Pt-NCs-x0.5-T700-t360.



Fig. S7 CV curves of CoFe@Pt-NCs-x0.5-T700-t360 and Pt/C normalized by ECSA in 0.5 M $\rm H_2SO_4$ at different scan rates.



Fig. S8 CV curves of CoFe-NCs-x0.5-T700 in 0.5 M H_2SO_4 + 0.5 M CH_3OH at the scan rate of 50

mV∙s⁻¹.



Fig. S9 TEM of (a) CoFe@Pt-NCs-x0.1-T700-t360, (b) CoFe@Pt-NCs-x0.3-T700-t360, (c) CoFe@Pt-NCs-x0.7-T700-t360, (d) CoFe@Pt-NCs-x1.0-T700-t360.



Fig. S10 CV curves of CoFe@Pt-NCs-xa-T700-t360 (a=0.1, 0.3, 0.7, 1.0) in 0.5 M $\rm H_2SO_4$ at the scan rate of 50 mV s^-1.



Fig. S11 CV curves of CoFe@Pt-NCs-xa-T700-t360 (a=0.1 (a), 0.3 (b), 0.7 (c), 1.0 (d)) in 0.5 M $H_2SO_4 + 0.5$ M CH₃OH solution at different scan rates.



Fig. S12 CV curves of (a) CoFe@Pt-NCs-xa-T700-t360 (a=0.1, 0.3, 0.7, 1.0) and (b) CoFe@Pt-NCs-x0.5-Tb-tc normalized by ECSA in 0.5 M H_2SO_4 at the scan rate of 50 mV·s⁻¹.



Fig. S13 Raman of CoFe@Pt-NCs-xa-T700-t360 (a=0.1, 0.3, 0.7, 1.0).



Fig. S14 Temperature-programmed reduction curves of (a) CFNPs, (b) PDA, (c) CFNPs-PDAx0.5.



Fig. S15 CV curves of CoFe@Pt-NCs-x0.5-Tb-tc in 0.5 M H₂SO₄.



Fig. S16 CV curves of CoFe@Pt-NCs-x0.5-Tb-tc (a) b=700, c=60; (b) b=700, c=20; (c) b=700, c=0; (d) b=600, c=0; (e) b=500, c=0; in 0.5 M H₂SO₄ + 0.5 M CH₃OH solution at different scan rates (scan rate: 75, 100, 125, 150, and 200 mV·s⁻¹).



Fig. S17 Deconvoluted XPS of Pt 4f for catalysts.



Fig. S18 Deconvoluted XPS of Co 2p for catalysts.



Fig. S19 Deconvoluted XPS of Fe 2p for catalysts.





Co⁰

Co-N、Co³⁺

40

20

0



Fig. S22 Temperature-programmed curves of CFNPs-PDA-x0.5.



Fig. S23 Temperature programmed curves of CFNPs-PDA-x0.5; (a) temperature setting routine, (b) temperature-programmed decomposition and reduction.



Fig. S24 XRD of CFNPs-PDA-x0.5 after temperature-programmed decomposition and reduction.



Fig. S25 TG/DTA of CFNPs-PDA-x0.5 after temperature programmed decomposition and reduction; (a) Ar, (b) Air.







Fig. S27 CV curves (a) CoFe@Pt-NCs-x0.5-T700-t0 and (b) Pt/C in 0.5 M H₂SO₄ + 0.5 M CH₃OH for 1000 Cycles. (c) Mass activity during 1000 cycles.



Fig. S28 CO stripping patterns recorded on CoFe@Pt-NCs-x0.5-T700-t0.

Catalyst	ECSA	Mass activity	Scan rate	Ref.	
	(m ^² g _{Pt} ^²)	(A mg _{Pt} ⁻¹)	(mV s ⁻¹)		
CoFe@Pt-NCs-X0.5-T700-t0	93.5	0.915	50	This work	
Hollow PtCu nanoparticles	49.24	0.755	50	Ref. ²	
PtRu/PANI/CNTs	N.A.	0.40	50	Ref. ³	
Hollow Pt@Ru Dodecahedra	76.2	0.80	20	Ref.⁴	
Pd@mPtAu CBs	39.3	0.54	50	Ref.⁵	
Ru/PtNWs	19.75	0.57	50	Ref. ⁶	
PtZn intermetallic nanoparticles	87.4	0.56	50	Ref. ⁷	
AuPtCu nanowires	N.A.	~0.50	50	Ref. ⁸	
FePtPd nanowires	N.A.	0.49	50	Ref. ⁹	
PtPd dendrites	N.A.	0.49	50	Ref. ¹⁰	
Pt/mesoporous carbon	N.A.	~0.45	20	Ref. ¹¹	
Pt/3D MoS ₂ -G	62.3	~0.0918	10	Ref. ¹²	
PtFe@PtRuFe core@shell nanoparticles	53	0.69	50	Ref. ¹³	
PtNi CNCs	N.A.	0.68	50	Ref. ¹⁴	
Octahedron Pt-Ag NCs	12.6	0.73	50	Ref.15	
Pt/CeO ₂ -P	N.A.	0.71	50	Ref. ¹⁶	
Pt/sulfur-doped multi-walled carbon nanotubes	161.4	0.80	50	Ref.17	

Table S2. Comparison of methanol oxidation behavior on the CoFe@Pt-NCs-X0.5-T700-t0 composite and various Pt-based electrocatalysts

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