Electronic Supplementary Information (ESI)

Highly dispersed ultrafine Pt nanoparticles on hydrophilic N-doped carbon tubes for improved methanol oxidation

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Experimental Section

Preparation of N-CT support

104 mg of ferric chloride hexahydrate ($FeCl_3•6H_2O$) was dissolved in 30 mL of ethanol aqueous solution ($V_{ethanol}:V_{H_2O} = 2:1$), and followed by adding 2 g lysine (as the carbon source) into the solution. The solution was sonicated for 20 min until the lysine was completely dissolved, then further mixed with 426 mg SiO_2 [13] to form a suspension, then sonicated for 2 h and the resulting mixture was dried at 80 °C overnight. The mixture was then heated to 300 °C at a rate 5 °C min^{-1} under N_2

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** Corresponding auther, e-mail: sji@uwc.ac.za, Tel/fax: +27-21-9599316 atmosphere for 1 h, and then heated to 900 °C for 1 h. The obtained solid products were ground into powders with an agate mortar. In order to remove SiO_2, the powders were immersed in HF solution ($V_{\text{HF solution}}$:V_{H_2O} = 1:1) for 24 h with stirring, then washed with deionized water and dried at 60 °C for 12 h to obtain N-CT.

Preparation of Pt/N-CT catalyst

77.4 mg of sodium citrate was dissolved in 30 mL ethylene glycol (EG) with sonication at room temperature, followed by the addition of 3.36 mL H_2PtCl_6 (20 mg mL^{-1}) solution and further sonication for 20 min, and the mixture was adjusted to ~pH 10 using a 5 wt% KOH/EG solution. The mixture was heated at 160 °C for 6 h and then cooled to the room temperature. 100 mg N-CT treated with 2 mol L^{-1} HNO_3 for 48 h was then added to the mixture (total metal loading: 20 wt%) and stirred overnight. The Pt/N-CT powder was collected by filtration, then washed with ethanol, deionized water, and finally dried in an oven at 40 °C for 12 h.

Physical characterization

X-ray diffraction (XRD) was carried out on a Shimadzu XD-3A (Japan), using filtered Cu-Kα radiation (40 kV, 30 mA). All X-ray diffraction patterns were analyzed using Jade 7.5 of Material Data, Inc. (MDI): peak profiles of individual reflections were obtained by a nonlinear least-square fit of the Cu-Kα corrected data. Scanning electron microscopy (SEM) images were carried out on a Carl Zeiss Ultra Plus microscope. Transmission electron micrographs (TEM) and selected area electron diffraction (SAED) patterns of the N-CN were taken on a JEOL (JEM-2000 FX) microscope operating at 200 kV. Raman spectra were obtained using Ft-Raman spectroscopy (RFS 100, BRU-KER) employing Nd: YAG laser operating at a wavelength of 1064 nm and a power of 100 mW. The elemental analysis of carbon (C) and nitrogen (N) were conducted using an organic elemental analyzer (Thermo Flash2000). The elemental composition of Pt/N-CT was investigated by EDX coupled to TEM. X-ray photoelectron spectroscopy (XPS) (Phi-5702 America) used a monochromatic Al Kα X-ray source ($h\nu$ = 1486.6 eV) was used.

Electrochemical characterization

Electrochemical measurements were carried out using an electrochemical workstation (CHI650D). A common three-electrode electrochemical cell system was used for the measurements. The counter and reference electrode were a platinum wire and an Ag/AgCl (saturated KCl solution) electrode respectively. The working electrode was a glassy carbon disk (5 mm in diameter). The thin-film electrode was prepared as follows: 5 mg of catalyst was dispersed ultrasonically in 1 mL Nafion/ethanol (0.25% Nafion) for 15 min. 8 μL of the dispersion was transferred onto the glassy carbon disk using a pipette, and then dried in air. All the experiments were conducted at ambient temperature. For comparison, commercial Pt/C with close metal loading (20%) was purchased from J. M. Corporation.

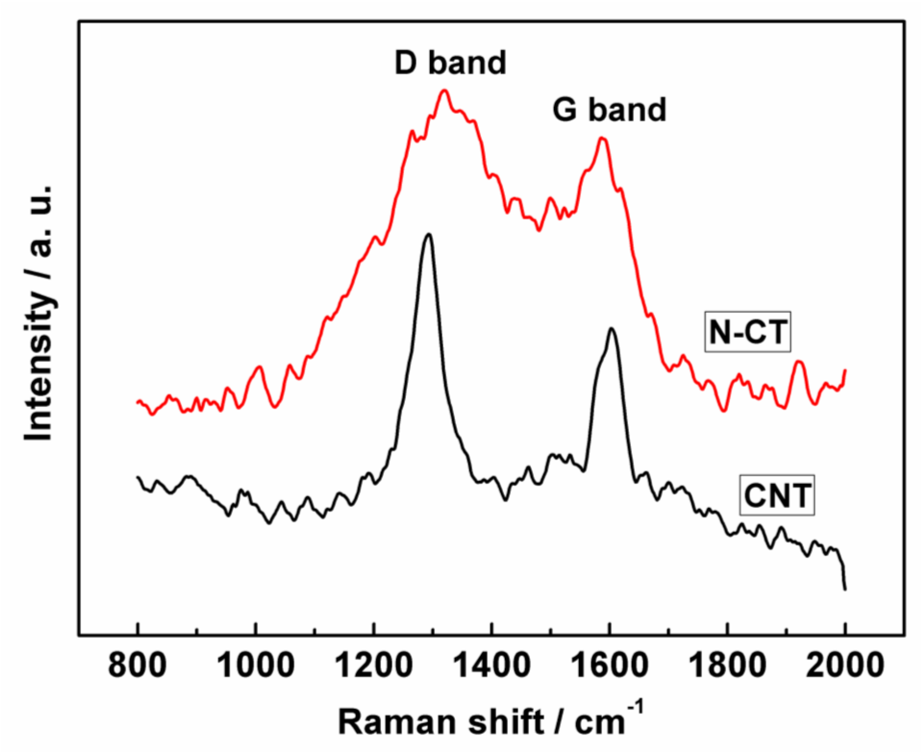

Fig. S1 Raman spectra of N-CT and CNT.

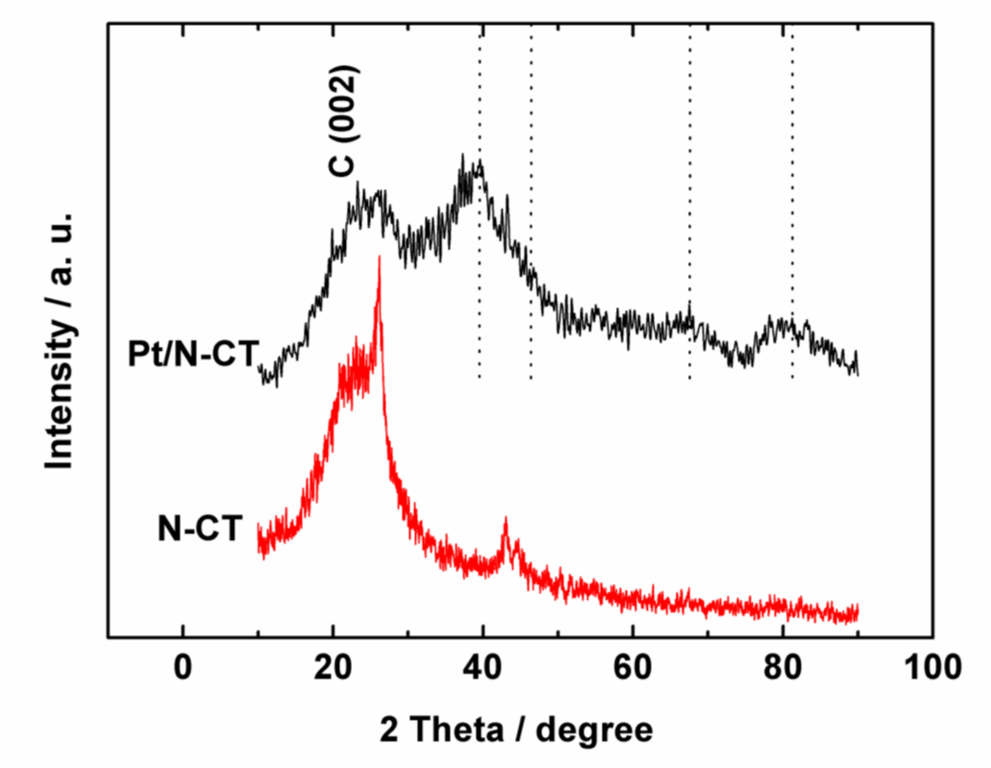

Fig. S2 XRD patterns of N-CT and Pt/N-CT.

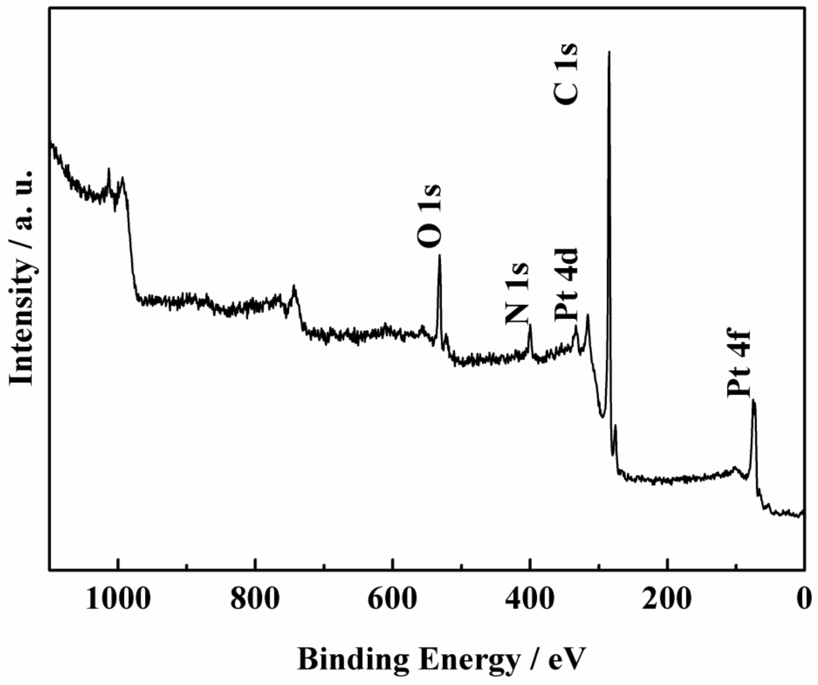

Fig. S3 XPS spectrum of Pt/N-CT.

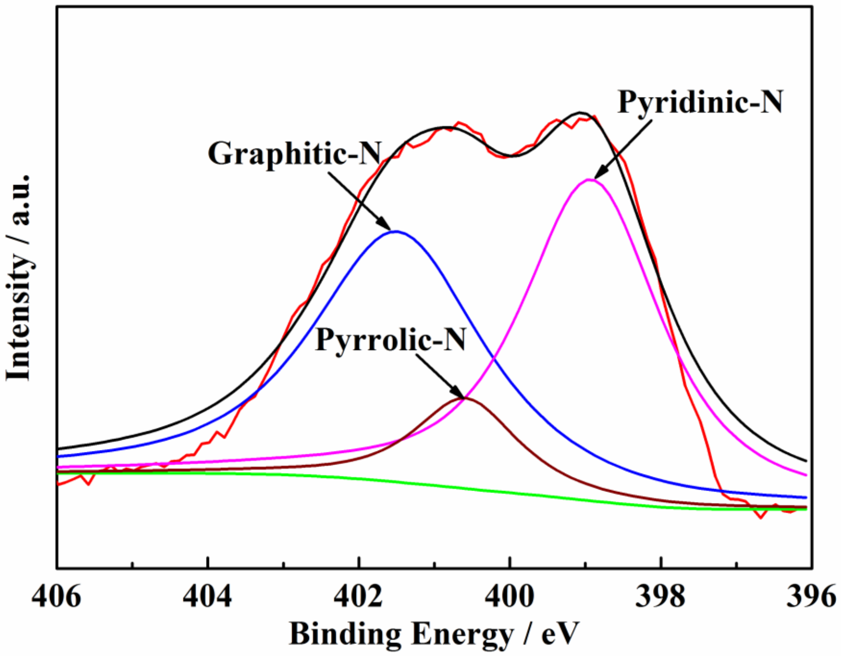

Fig. S4 N 1s region of N-CT.

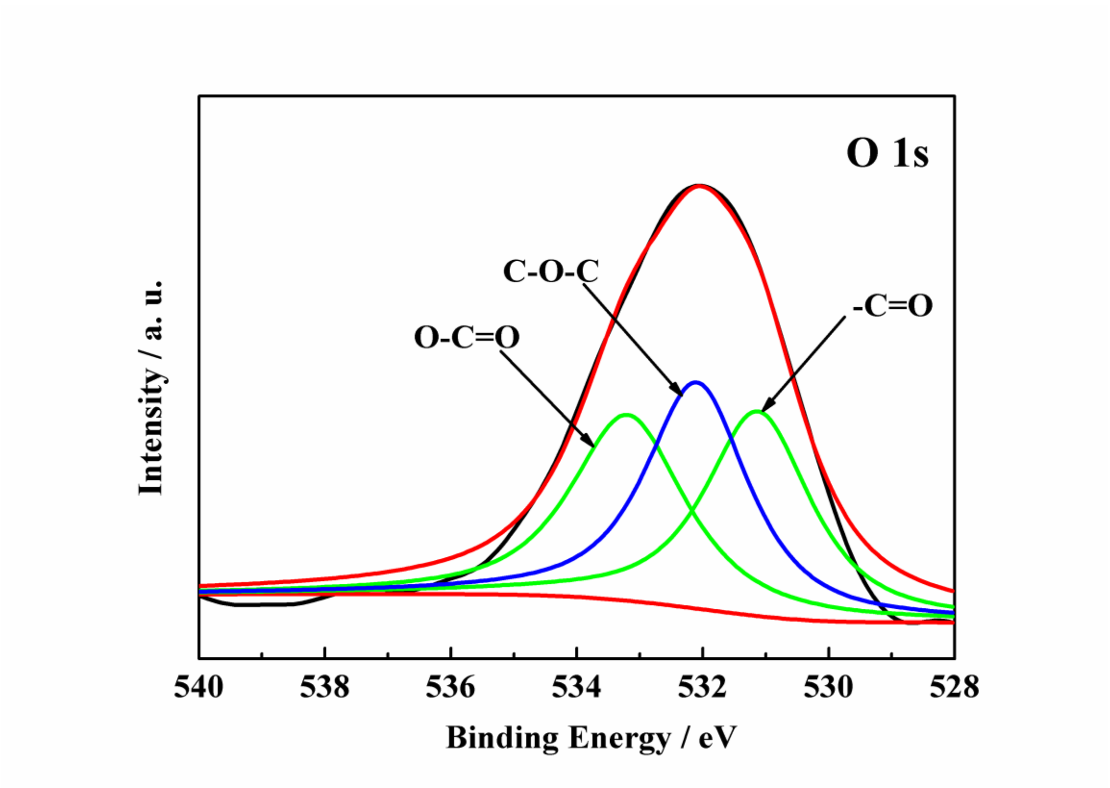

Fig. S5 O 1s region of Pt/N-CT.

Table S1 The binding energies and atom ratio (%) of Pt(0), Pt(Ⅱ) and Pt(Ⅳ) at Pt 4f$_{7/2}$ of different platinum species.

Catalyst	Pt 4f$_{7/2}$ (eV)			Atom ratio (%)		
	Pt(0)	Pt(Ⅱ)	Pt(Ⅳ)	Pt(0)	Pt(Ⅱ)	Pt(Ⅳ)
Pt/N-CT	72.3	73.1	71.7	87.5	8.3	4.2
Pt/C	71.2	72.1	70.7	65.0	19.4	15.6

Table S2 Summary of the electrochemical performance of Pt/N-CT and Pt/C catalysts.

Catalyst	Pt/N-CT	Pt/C
$ECSA_{\mathrm{H}}$ ($m^2\ g^{-1}{}_{\mathrm{Pt}}$)	139.7	106.8
The onset potential of methanol oxidation (V)	0.14	0.22

The peak potential of methanol oxiatation (V)	0.65	0.67
The current density of methanol oxidation (mA $mg^{-1}{}_{Pt}$)	566	277
The onset potential of CO oxidation (V)	0.58	0.62
The peak potential of CO oxidation (V)	0.66	0.69
$ECSA_{CO}$ (m^2 $g^{-1}{}_{Pt}$)	179.4	127.8

References

1. R. Wang, X. Li, H. Li, Q. Wang, H. Wang, W. Wang, J. Kang, Y. Chang and Z. Lei, *Int. J. Hydrogen Energy*, 2011, **36**, 5775-5781.