Electronic Supplementary Information

Pyrolysis of Conjugated Nanoporous Polycarbazoles to Mesoporous N-doped Carbon Nanotubes as Efficient Electrocatalysts for Oxygen Reduction Reaction

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Material characterization: The morphology of the samples was characterized by using a JEOL JEM-2100 transmission electron microscopy (TEM). The powder X-ray diffraction (PXRD) data were carried out on a D/Max2550 VB/PC diffractometer (40 kV, 200 mA) using a Cu Kα as the radiation. The FT-IR spectra were recorded on a Nicolet iS10 FTIR spectrometer using the KBr pellet technique. Gas adsorption/desorption isotherms were measured by volumetric adsorption analyzer ASAP 2020 and 3020 after the samples were degassed at 150 °C for 12 h under vacuum. Brunauer-Emmett-Teller (BET) and t-plot model were used to determine the specific surface area and t-plot micropore area of the samples, respectively. The total pore volume of the samples was estimated at a relative pressure of $P/P_0 = 0.99$. Pore size distributions (PSDs) were calculated using nonlocal density functional theory (NLDFT). CO₂ adsorption isotherms were measured up to 1 atm at 273 and 298 K. The thermal decomposition behavior of the sample was performed on a NETZSCH STA 499 F3 thermogravimetric analyzer, and the sample was heated at a rate of 10 °C min⁻¹ under N₂ gas flow at a rate of 40 mL min⁻¹. Elemental analysis was conducted on an elemental analyzer (Vario EL III). Solution ¹H nuclear magnetic resonance (NMR) spectrum was obtained in a CDCl₃ solution with a Bruker 400MHz Advance spectrometer. Solid state ¹³C cross-polarization (CP)/magic-angle spinning (MAS) NMR spectrum was recorded with a Bruker Avance III- 600MHz spectrometer at a frequency of 100.62 MHz with 13 kHz spinning rate, and 1024 scans were signal averaged. The chemical shifts of ¹³C NMR spectra were referenced to tetramethylsilane. Fe containing was measured by inductively coupled plasma atomic emission spectrometry (ICP-OES, Agilent 725ES).

Catalyst ink preparation and electrochemical measurements: The catalyst ink was prepared by dispersing 3 mg of the catalyst into the 900 μ L ethanol containing 100 μ L 5 % Nafion in an ultrasonic bath to form a homogeneous ink (3 mg mL⁻¹). The glassy carbon electrode with a surface area of 0.196 cm² (Pine Instruments, USA) was polished using aqueous alumina suspensions on felt polishing pads prior to use. Then, 10 μ L of the ink was deposited on the glassy carbon electrode with an overall catalyst loading of 0.15 mg cm⁻². The resulting electrode was dried under ambient conditions. For comparison, commercial a Pt/C catalyst (20 wt% Pt, JM) with the same degree of loading as the 0.15 mg cm⁻² sample was prepared, except that positive scan was recorded to avoid performance loss caused by anions adsorption.¹ CV (using a CHI 760e) was conducted in a three-electrode electrochemical cell with a Pt counter

electrode, an Ag/AgCl reference electrode (3 M KCl) and with 0.1 M KOH or HClO₄ as the electrolyte. The potential, measured against an Ag/AgCl electrode, was converted to the potential versus the reversible hydrogen electrode (RHE) on the potential cycle measured at a scan rate of 1mV s⁻¹ in H₂-saturated 0.1 M KOH or HClO₄.¹ The onset potential has been defined as a potential required for generating an ORR current density of 0.1 mA cm⁻² in a steady-state RDE experiment.² Prior to the start of each experiment, electrolyte was saturated with O₂ by bubbling O₂. A flow of O₂ was retained over the electrolyte during the measurements of CVs to ensure its continued O₂ saturation. The working electrode was cycled at least 10 times before data were recorded at a scan rate of 10 mV s⁻¹.

Rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) measurements: For RDE measurements, catalyst inks were prepared by the same method as for CV. RDE tests were measured in O_2 -saturated 0.1 M KOH or HClO₄ with varying rotating speed from 400 to 1600 rpm at a sweep rate of 5 mV s⁻¹. All ORR currents shown in the figures are Faradaic currents, that is, after correction for the capacitive current. The exact kinetic parameters like electron transfer number (n) and kinetic current density (J_k) involved in the typical ORR process were analyzed according to the Koutecky-Levich (K-L) equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$
(1)

$$B = 0.2nFC_0 (D_0)^{2/3} v^{-1/6}$$
⁽²⁾

J, J_L , J_k are the measured current density, the diffusion current density, and the kinetic current density, respectively. ω is the rotation speed in rpm, F is the Faraday constant (96485 C mol⁻¹), D_0 is the diffusion coefficient of oxygen in 0.1 M KOH (1.9×10⁻⁵ cm² s⁻¹), v is the kinetic viscosity (0.01 cm² s⁻¹), and C₀ is the bulk concentration of oxygen (1.2×10⁻⁶ mol cm⁻³). The constant 0.2 is adopted when the rotation speed is expressed in rpm.

For detecting peroxide species formed at the disc electrode, the potential of the Pt ring electrode in the RRDE system was set to 1.4 V versus RHE.¹ The hydrogen peroxide yield (%H₂O₂) and the electron transfer number (n) were obtained from the following equations:

%
$$H_2O_2 = 200 \times \frac{I_R/N}{I_D + I_R/N}$$

$$n = 4 \times \frac{I_D}{I_D + I_R / N} \tag{4}$$

Where I_D and I_R are the disk and ring currents, respectively. N is the ring current collection efficiency which was determined to be 37 % by the reduction of 10 mM K_3 [Fe(CN)₆] in 0.1 M KNO₃.

Figures:



Fig. S1. $^{1}H\rightarrow ^{13}C$ CP/MAS NMR spectra of **Py-PCz**.



Fig. S2. Thermogravimetric analysis of Py-PCz.



Fig. S3. Raman spectra of the obtained N-CNT-based catalysts.



Fig. S4. Low-angle (a) and wide-angle (b) XRD of N-CNT-Xs.



Fig. S5. TEM images of N-CNT-800 (a), N-CNT-900 (b) and N-CNT-1000 (c), respectively.



Fig. S6. High-resolution N 1s spectra of N-CNT-800 (a), N-CNT-900 (b), N-CNT-1000 (c) and N-CNT-900-NH₃ (d).



Fig. S7. Nitrogen adsorption-desorption isotherms (a) and the corresponding BJH pore size distribution (b) of **N-CNT-900-NH**₃, respectively.



Fig. S8. ORR polarization plots of **N-CNT-X-NH**₃ in O₂-saturated 0.1 M KOH. Electrode rotation speed, 1600 rpm.



Fig. S9. RDE polarization curves on **N-CNT-900-NH₃** at different rotation rates in O₂-saturated 0.1 M KOH.



Fig. S10. Tafel plots of N-CNT-900-NH₃ and Pt/C in 0.1 M KOH.



Fig. S11. Electrochemical impedance spectroscopy (EIS) analyses of the **N-CNT-Xs**. EIS were recorded in O_2 -saturated 0.1 M KOH at 0.85 V vs RHE with 5 mV ac potential from 100 kHz to 0.01 Hz. The loading was 0.15 mg/cm² for all materials. Electrode rotation speed is 1600 rpm.



Fig. S12. CVs in O_2 -saturated 0.1 M KOH and O_2 -saturated 0.1 M KOH upon the addition of CH₃OH (1.0 M) for N-CNT-900-NH₃ (a) and the Pt/C (b).



Fig. S13. CVs in O_2 -saturated 0.1 M HClO₄ and O_2 -saturated 0.1 M HClO₄ with 1.0 M CH₃OH for **N-CNT-900-NH₃** (a) and the Pt/C (b).



Fig. S14. ¹HNMR spectrum of 3,5-di(9H-carbazol-9-yl)pyridine (3,5-CzPy).

Sample	S bet	S micro	V _{total}	V micro	
-	(m ² /g)	(m ² /g)	(cm ³ /g)	(cm ³ /g)	
Py-PCz	1222	502	1.03	0.26	
N-CNT-800	750	655.0	0.51	0.32	
N-CNT-900	793	673.3	0.54	0.32	
N-CNT-1000	811	707.5	0.55	0.34	
N-CNT-900-NH ₃	1171	924.0	0.79	0.44	

Table S1. Textural parameters of Py-PCz and N-CNT catalysts.

Catalysts	C at	O at	Fe at	Fe wt	Total	Pyridinic	Pyrrolic	Quaternary
	%	%	% ⁰a	% ⁰	N at %	N at %	N at %	N at %
N-CNT-800	91.68	4.25	0.00	—	4.07	8.8	36.6	54.5
N-CNT-900	92.81	4.24	0.00	0.36	2.94	34.0	12.2	53.7
N-CNT-1000	94.64	3.32	0.00	—	2.04	7.0	2.9	90.1
N-CNT-900-NH ₃	95.11	2.92	0.00	0.67	1.97	12.2	5.6	82.2

 Table S2. Summary of chemical compositions of N-CNT-Xs.

^a Fe contents was measured by XPS. ^b Fe contents was measured by ICP-OES and the average value was obtained by three times parallel determiniation.

Table S3. Summary of ORR performance for carbonaceous catalysts in alkaline and acidic media.

N-CNT Catalyst	Loading (mg cm ⁻²)	Electrolyte	Onset potential (V)	Half-wave potential (V)	Half-wave potential of Pt/C (V)	ΔE (mV) ^a	Ref
N-CNT-900-NH ₃	0.15	0.1 M KOH	1.02	0.88	0.86	+22	This work
Pt/C	0.15	0.1 M KOH	0.99	0.86	_	_	This work
CoP-CMP800	0.15	0.1 M KOH	0.852	0.792	0.805	-13	3
TTF-F	unknown	0.1 M KOH	0.86	0.767	0.78	-13	4
PCN-FeCo/C	0.2	0.1 M KOH	1.00	0.85	0.84	+10	5
C-COP-P-Fe	0.2	0.1 M KOH	0.98	0.77	0.80	-30	6
Fe-N/C-800	0.1	0.1 M KOH	0.923	0.809	0.818	-9	7
Fe ₃ C/NG-800	0.4	0.1 M KOH	1.03	0.86	0.83	+30	8
PMF-800	1.2	0.1 M KOH	1.02	0.861	0.812	+49	9
IAG-C	0.3	0.1 M KOH	1.02	0.87	0.85	+20	10
N-Fe-CNT/CNP	0.2	0.1 M NaOH	1.08	0.87	0.91	-40	11
FeCo-OMPC	0.3	0.1 M KOH	unknown	0.86	0.86	0	12
N-CNT-900-NH ₃	0.6	0.1 M HClO ₄	0.923	0.76	0.84	-80	This work
Pt/C	0.15	0.1M HClO ₄	0.96	0.84	_	_	This work
CoP-CMP800	0.15	0.5 M H ₂ SO ₄	0.74	0.64	0.789	-149	3

PCN-FeCo/C	0.6	0.1 M HClO ₄	0.90	0.76	0.78	-20	5
C-COP-P-Fe	0.2	0.1 M HClO ₄	0.89	0.57	0.62	-50	6
Fe-N/C-800	0.1	0.1 M HClO ₄	0.81	0.59	0.649	-59	7
Fe ₃ C/NG-800	0.4	0.1 M HClO ₄	0.92	0.77	0.84	-70	8
PMF-800	1.2	$0.5 \mathrm{~M~H_2SO_4}$	0.886	0.62	0.78	-160	9
FeCo-OMPC	1.52	0.1 M HClO ₄	1.000	0.845	0.840	+5	12
VB12/Silica colloid	0.6	0.5 M H ₂ SO ₄	0.93	0.79	0.848	-58	13
PmPDA-FeN _x /C	0.6	$0.1 \mathrm{~M~H_2SO_4}$	0.94	0.82	0.885	-65	14
Fe ₃ C/C-700	0.6	0.1 M HClO ₄	0.9	0.73	0.83	-100	15
PpPD-Fe-C	0.9	$0.5 \mathrm{~M~H_2SO_4}$	0.826	0.718	0.807	-89	16

^a $\Delta E = E_{1/2}$ (catalyst)- $E_{1/2}$ (Pt/C)

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