

Supplementary Information for

Highly Efficient Metal-Free Electrocatalysts toward Oxygen Reduction Derived from Carbon Nanotubes@Polypyrrole Core-Shell Hybrids

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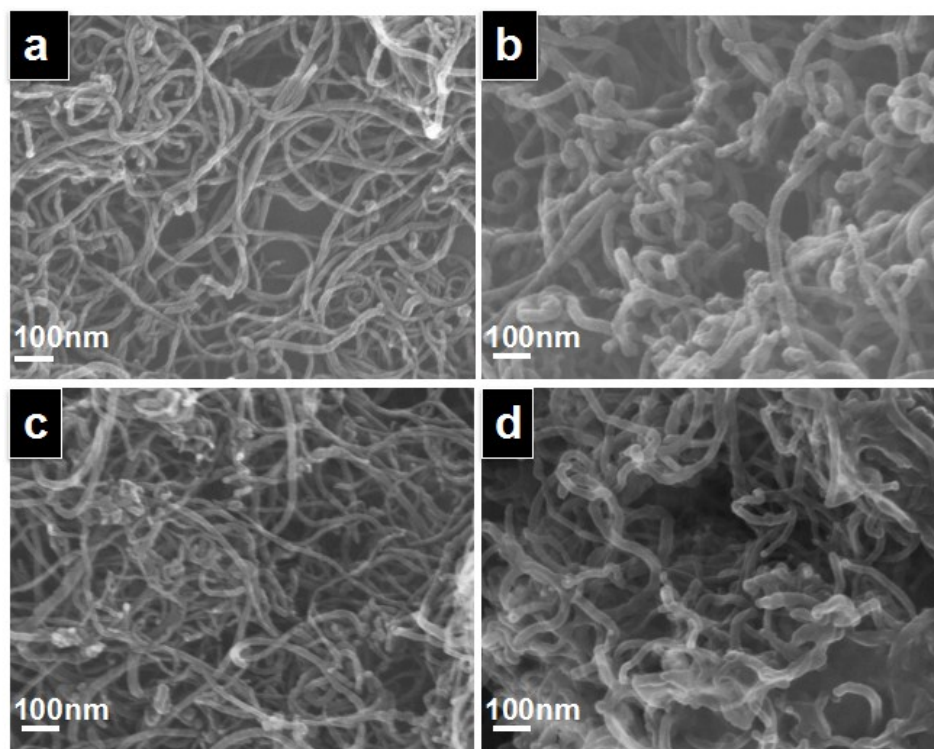


Fig. S1 SEM images of (a) CNTs, (b) CNTs@PPy, (c) CNTs-P800, and (d) CNTs@PPy-P800, respectively.

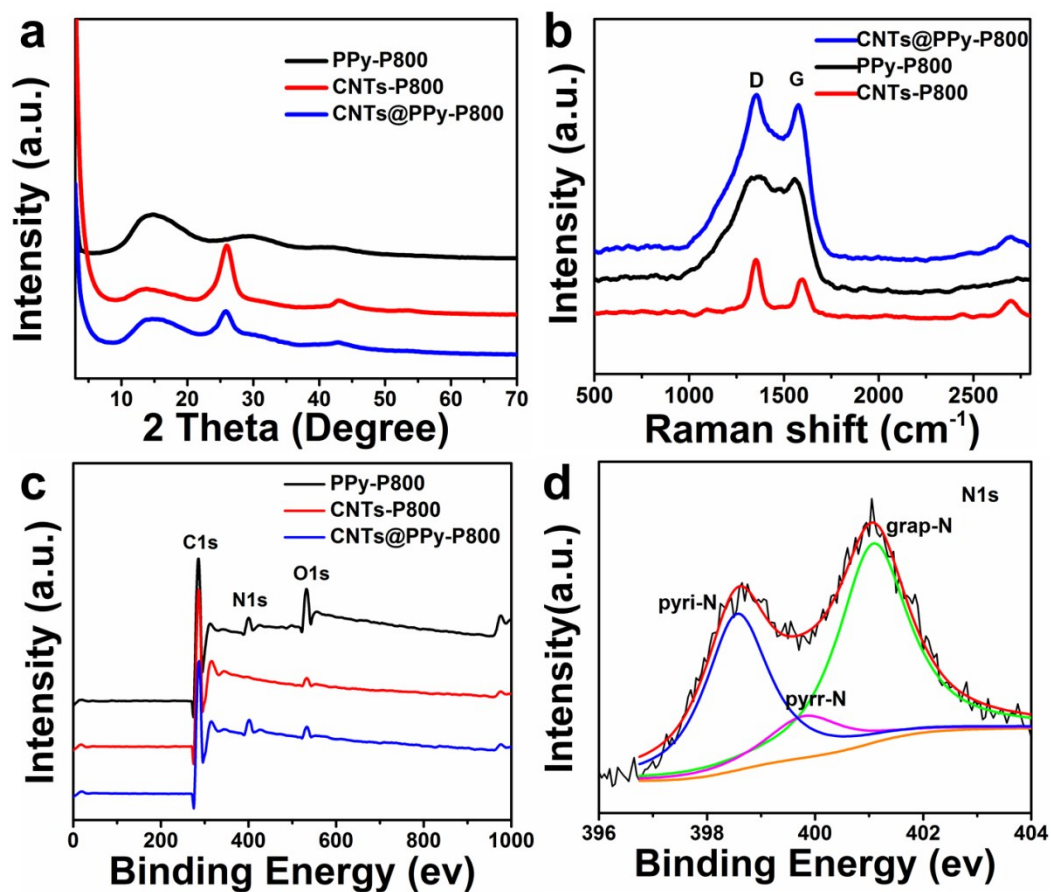


Fig. S2 (a) XRD patterns of PPy-P800, CNTs-P800, and CNTs@PPy-P800. (b) Raman spectra of CNTs-P800, PPy-P800, and CNTs@PPy-P800. (c) XPS survey spectra of PPy-P800, CNTs-P800, and CNTs@PPy-P800. (d) High resolution scans of N1s for CNTs@PPy-P800.

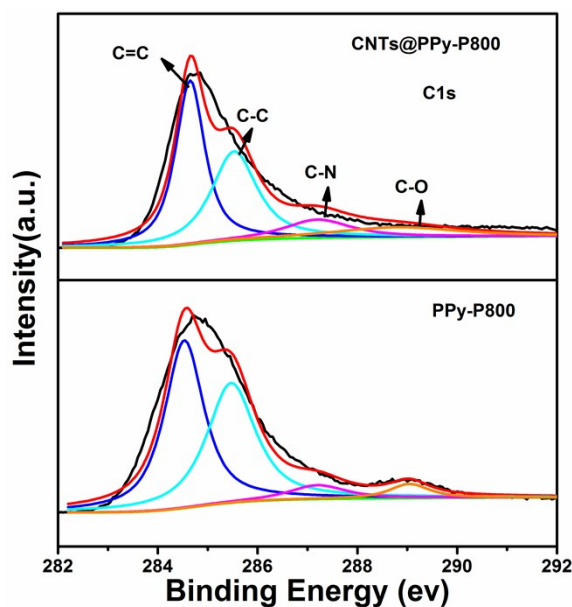


Fig. S3 High resolution scans of C1s for the PPy-P800 and CNTs@PPy-P800.

Table S1. Percentage of various carbon species as a function of PPy-P800 and CNTs@PPy-P800.

Sample	C=C(%)	C-C(%)	C-N(%)	C-O(%)
PPy-P800	48.02	42.33	5.64	4.01
CNTs@PPy-P800	42.61	35.84	10.73	10.82

Table S2. Comparison of the onset potential, half-wave potential and current density for CNTs-P800, PPy-P800, CNTs@PPy-P800, and Pt/C

Sample	E_{onset} vs. RHE (V)	$E_{1/2}$ vs. RHE (V)	Current density (mA cm^{-2} at 0.2V)
CNTs-P800	0.82	0.65	3.36
PPy-P800	0.78	0.58	4.00
CNTs@PPy-P800	0.95	0.81	6.82
Pt/C	0.94	0.80	4.94

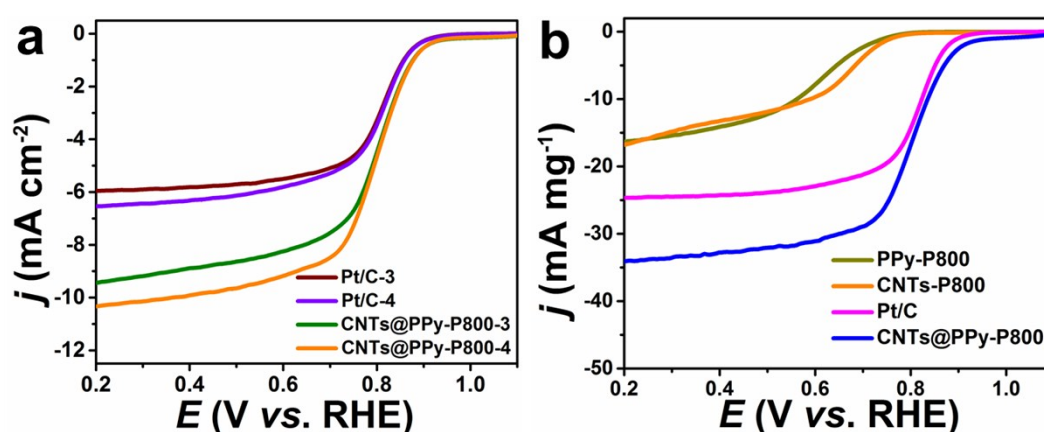


Fig. S4 (a) LSV curves of CNTs@PPy-P800, and Pt/C with different catalyst loading (3 mg cm^{-2} , 4 mg cm^{-2}). (b) LSV curves of PPy-P800, CNTs-P800, CNTs@PPy-P800,

and Pt/C catalyst in O₂-saturated 0.1 M KOH solution at a sweep rate of 10 mV s⁻¹ and electrode rotation speed of 1600 rpm.

Table S3. Current density at 0.2 V for CNTs@PPy-P800 and Pt/C with different catalyst loading (0.2mg cm⁻², 0.3mg cm⁻², 0.4mg cm⁻²)

Sample	0.2mg cm ⁻²	0.3mg cm ⁻²	0.4mg cm ⁻²
Pt/C	4.94 mA cm ⁻²	5.98 mA cm ⁻²	6.54 mA cm ⁻²
CNTs@PPy-P800	6.82 mA cm ⁻²	9.42 mA cm ⁻²	10.32 mA cm ⁻²

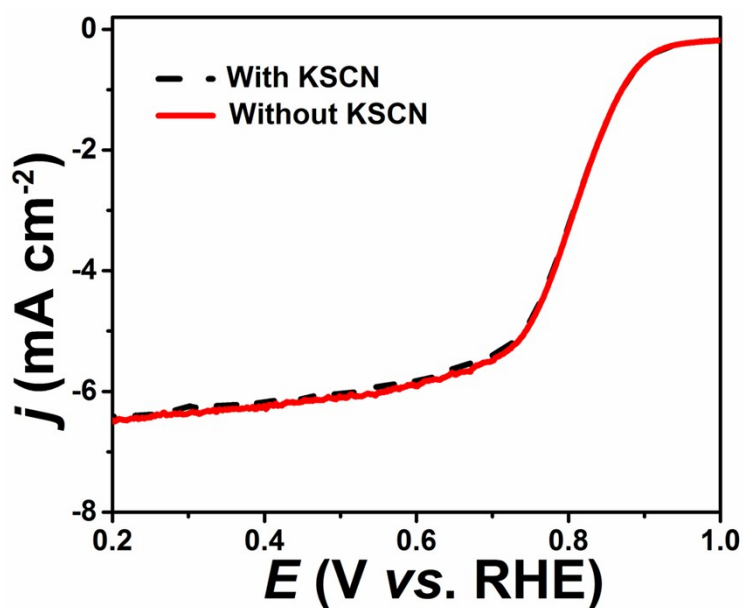


Fig. S5 LSV curves for CNTs@PPy-P800 without and with 10 mM KSCN.

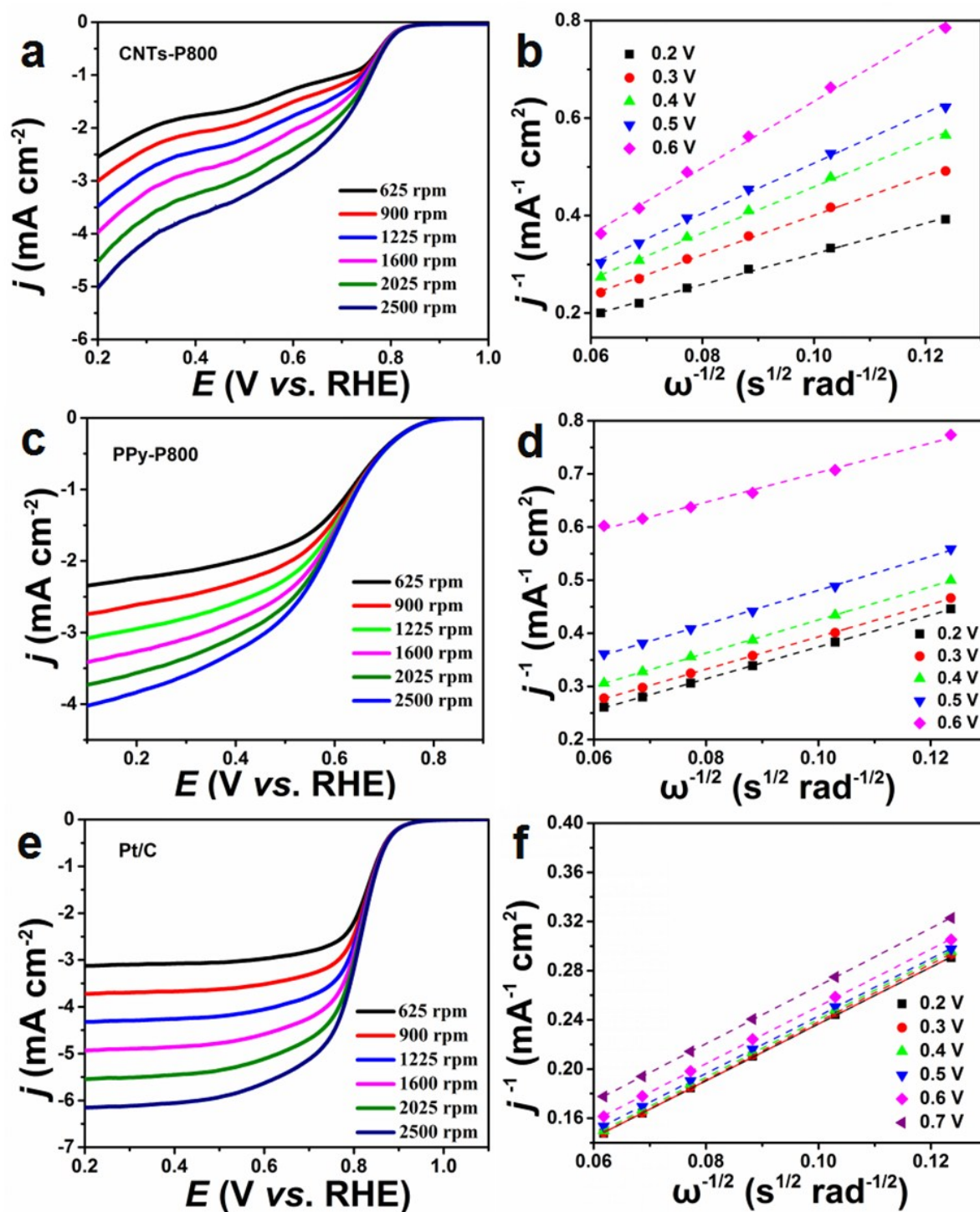


Fig. S6 LSV curves for (a) CNTs-P800, (c) PPy-P800, and (e) Pt/C at the rotation rates of 625 to 2500 rpm, respectively. The corresponding K-L plots derived from the RDE data for (b) CNTs-P800, (d) PPy-P800, and (f) Pt/C, respectively.

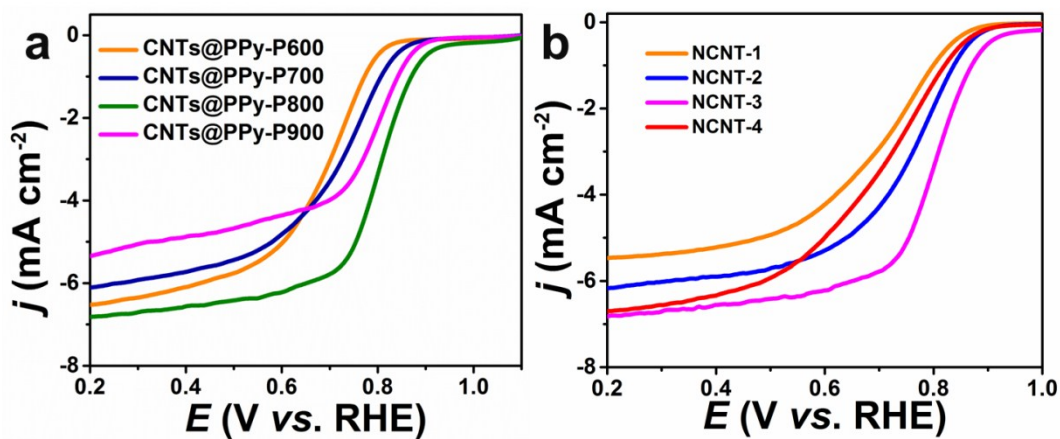


Fig. S7 (a) LSV curves of CNTs@PPy-*T* (*T* = 600, 700, 800, 900 °C, respectively).
 (b) LSV curves of NCNT-*x* (*x* = 1, 2, 3 and 4, respectively)

Table S4. Comparison of the onset potential, half-wave potential and current density for CNTs@PPy-*T* (*T* = 600, 700, 800, 900 °C, respectively) obtained in this work

Sample	E_{onset} vs. RHE (V)	$E_{1/2}$ vs. RHE (V)	Current density (mA cm ⁻² at 0.2V)
CNTs@PPy-P600	0.83	0.69	6.51
CNTs@PPy-P700	0.87	0.72	6.12
CNTs@PPy-P800	0.95	0.81	6.82
CNTs@PPy-P900	0.89	0.77	5.30

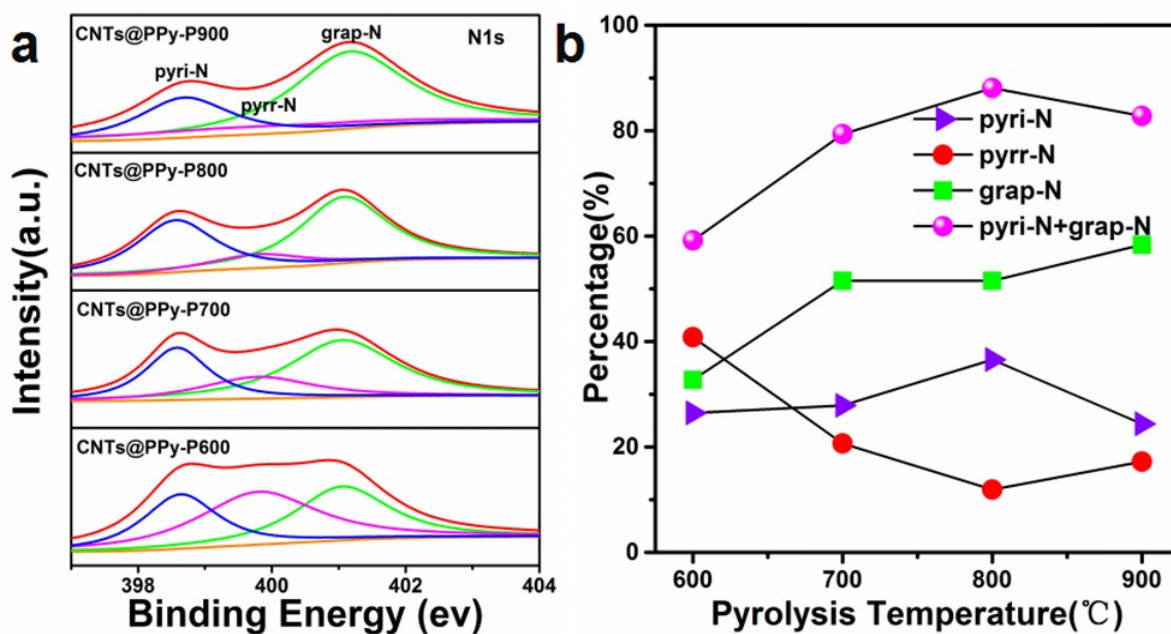


Fig. S8 (a) N1s XPS spectra and (b) Percentage of various nitrogen species of CNTs@PPy-*T* (*T* = 600, 700, 800 and 900 °C, respectively).

Table S5. Percentage of various nitrogen species as a function of pyrolysis temperature.

Sample	pyri-N/ N_{total} (%)	pyrr-N/ N_{total} (%)	grap-N/ N_{total} (%)	(pyri-N+grap-N)/ N_{total} (%)
CNTs@PPy-P600	26.45	40.8	32.75	59.2
CNTs@PPy-P700	27.85	20.64	51.51	79.36
CNTs@PPy-P800	36.58	11.89	51.53	88.11
CNTs@PPy-P900	24.39	17.24	58.37	82.76

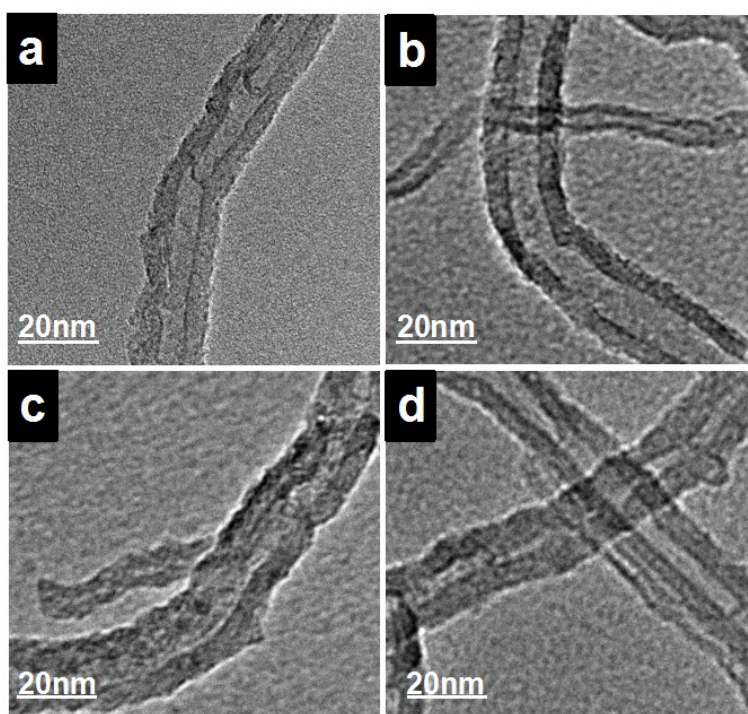


Fig. S9 HRTEM images of (a) NCNT-1, (b) NCNT-2, (c) NCNT-3, and (d) NCNT-4.

Table S6. Comparison of the onset potential, half-wave potential and current density for NCNT-x (x= 1, 2, 3 and 4, respectively)

Sample	E_{onset} vs. RHE (V)	$E_{1/2}$ vs. RHE (V)	Current density (mA cm^{-2} at 0.2V)
NCNT-1	0.87	0.71	5.5
NCNT-2	0.90	0.78	6.2
NCNT-3	0.95	0.81	6.82
NCNT-4	0.9	0.73	7.25

Table S7. The elements content of NCNT-x (x= 1, 2, 3 and 4, respectively)

Sample	C(%)	O(%)	N(%)
NCNT-1	93.08	4.86	2.06

NCNT-2	91.00	3.65	5.35
NCNT-3	88.50	4.59	6.90
NCNT-4	88.14	3.97	7.89

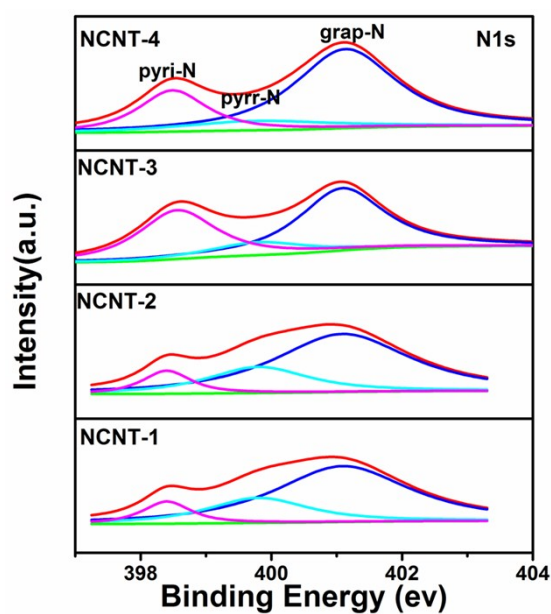


Fig. S10 (a) N1s XPS spectra of NCNT-x (x= 1, 2, 3 and 4, respectively).

Table S8. Percentage of various nitrogen species of NCNT-x (x= 1, 2, 3 and 4, respectively)

Sample	pyri-N/ N_{total} (%)	pyrr-N/ N_{total} (%)	grap-N/ N_{total} (%)	(pyri-N+grap-N)/ N_{total} (%)
NCNT-1	9.68	22.85	67.47	77.15
NCNT-2	12.15	21.92	65.93	78.08
NCNT-3	36.58	11.89	51.53	88.11
NCNT-4	22.92	11.9	65.17	88.10

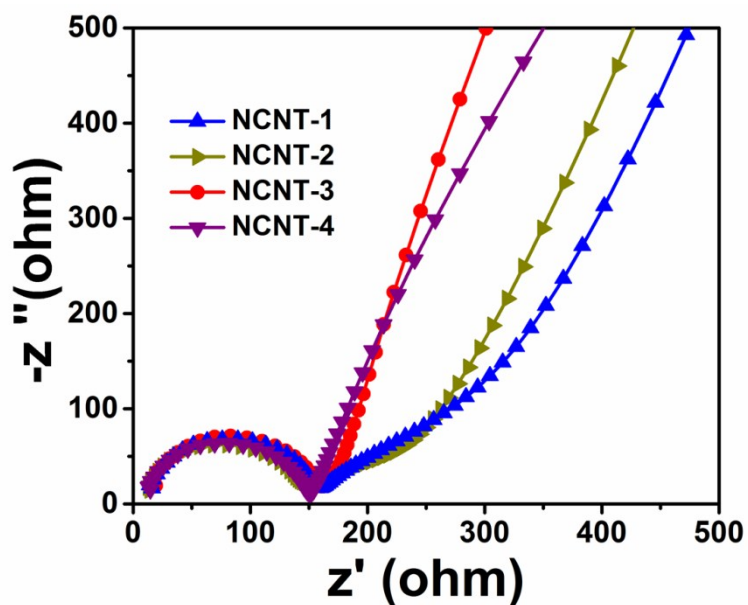


Fig. S11 EIS spectra of NCNT-x (x= 1, 2, 3 and 4, respectively).

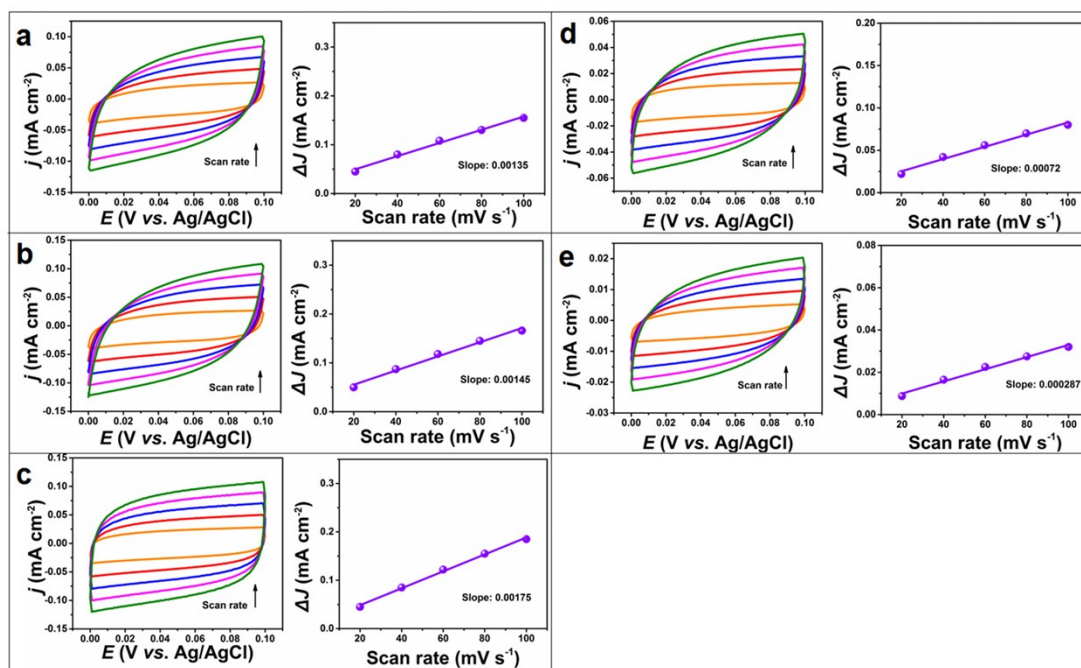


Fig. S12 CV curves at various scan rates (20, 40, 60, 80 and 100 mV/s) in the potential range 1–1.1 V vs. RHE for NCNT-x (x= 1, 2, 3 and 4, respectively) and CNT-P800 catalyst in 0.1 M KOH.

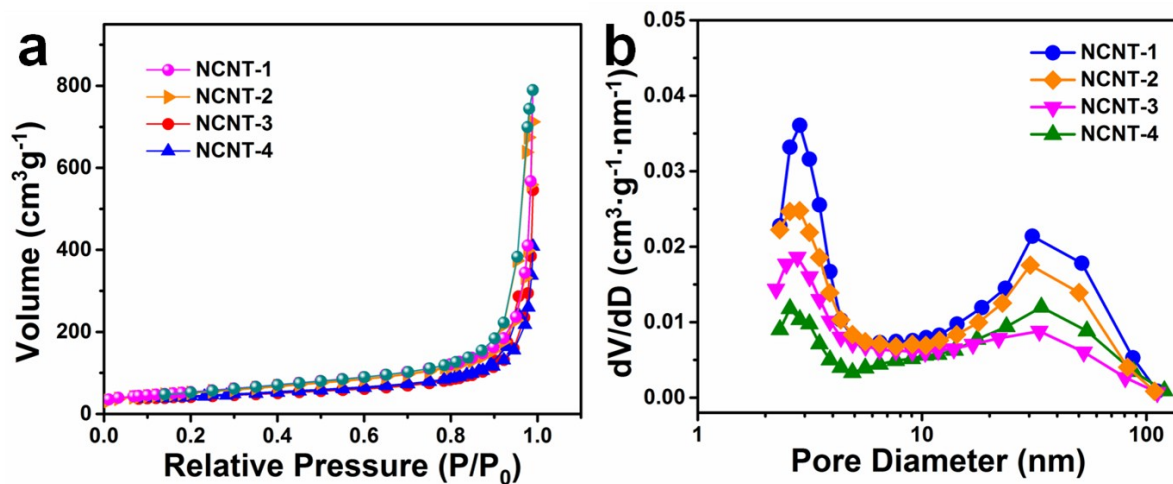


Fig. S13 (a) N₂ sorption isotherms and (b) the pore size distribution of NCNT-*x* (*x*= 1, 2, 3 and 4, respectively).

Table S9. The surface area of NCNT-*x* (*x*= 1, 2, 3 and 4, respectively)

Sample	BET surface area (m ² g ⁻¹)
NCNT-1	192.47
NCNT-2	181.91
NCNT-3	151.02
NCNT-4	149.46

Table S10. ORR performance of different catalysts (the electrolyte is 0.1 M KOH)

Catalyst	Loading (mg cm ⁻²)	E _{onset} vs. RHE (V)	E _{1/2} vs. RHE (V)	Current density (mA cm ⁻² at 0.4V)	Ref.
N-doped CNT arrays	Unknown	0.96	/	/	S1
N-doped CNTs	0.204	0.853	0.654	/	S2
EDA-NCNT	Unknown	0.94	0.81	4.91	S3

Winged N-doped CNTs	0.222	0.93	0.79	4.24	S4
N-CNT-1030	0.0813	0.91	0.694	4.80	S5
N-doped 3D GFs	0.012	0.78	/	1.20	S6
CNT@NCNT	0.025	0.94	/	/	S7
N-Carbon nanosheets	0.6	0.954	0.834	5.11	S8
CNTs@PPy-P800	0.2	0.95	0.81	6.72	This work

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