

Low-cost chitosan-derived N-doped carbons boost electrocatalytic activity of multi-wall carbon nanotubes

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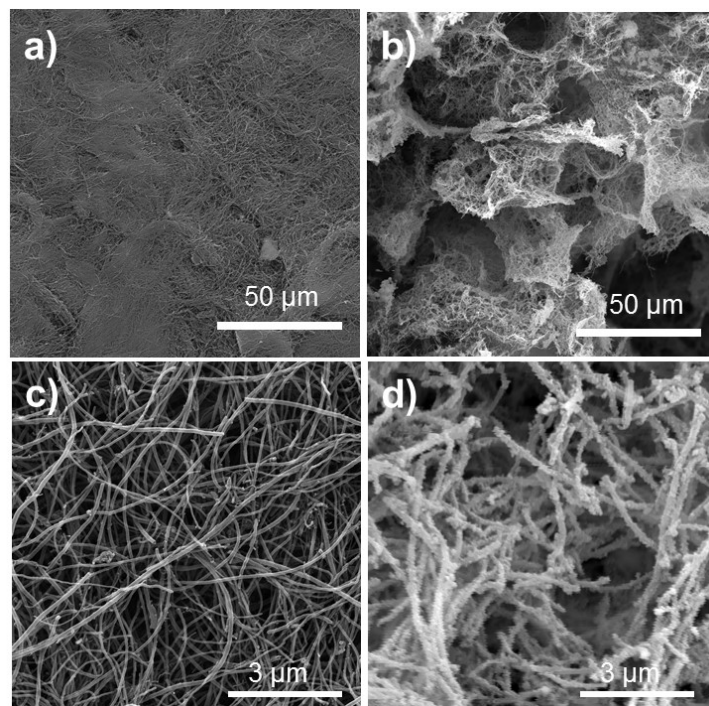


Figure S1 SEM images of samples after HTC process at 200 °C for 12 h: a, c) pure MWCNTs after HTC process, and b, d) chitosan-MWCNT hybrids (NC-CNT) synthesized via hydrothermal carbonization (HTC) process of MWCNT and chitosan mixture. Compared with pure MWCNT, the NC-CNT hybrids demonstrated similar tubular structure with larger diameter and more distinct 3-D network structure.

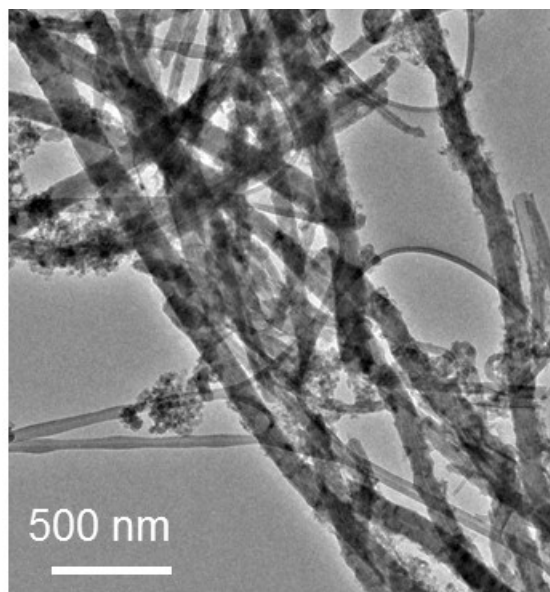


Figure S2 Low resolution TEM images of NC-CNT-1000 in Fig. 1c: tubular structure of the hybrids and the distribution of nitrogen-doped carbon derived from chitosan was demonstrated on MWCNTs surface.

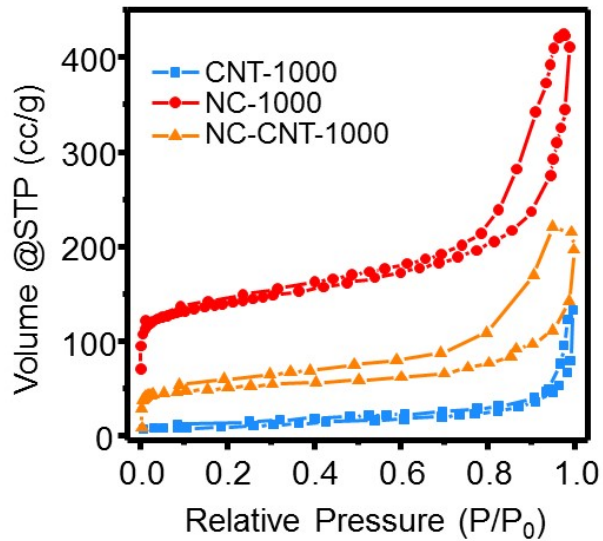


Figure S3 The N₂ sorption isotherms of samples synthesized from: pure MWCNT (CNT-1000), pure chitosan (NC-1000) and chitosan-MWCNT hybrids (NC-CNT-1000) via sequent treatment of HTC and annealing process at 1000°C for 2 h at N₂ atmosphere.

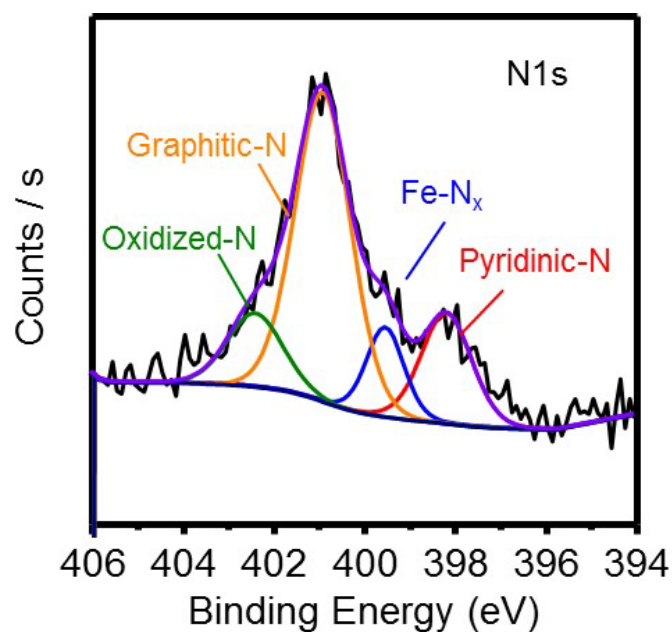


Figure S4 The XPS N 1s spectra of NC-CNT-1000: distribution of pyridinic-N, Fe-N_x, and graphitic-N was illustrated at the binding energy of 398.2 eV, 399.6 eV and 400.9 eV, respectively.

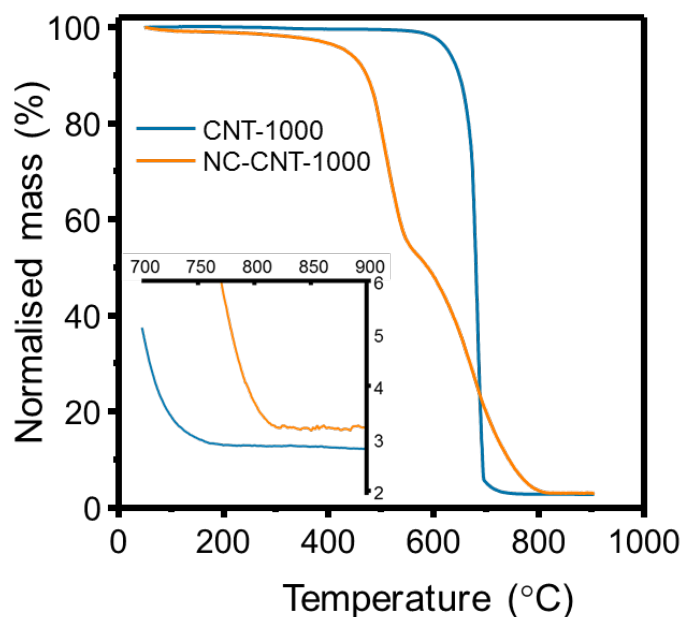


Fig S5 The TGA result of CNT-1000 and NC-CNT-1000: The NC-CNT-1000 showed two distinct drops which proved the amorphous/graphitic dual nature of the hybrid structure. The mass residual of 2.8 wt% and 3.2 wt% for CNT-1000 and NC-CNT-1000 demonstrated the iron content of 2.0 wt% and 2.3 wt% in CNT-1000 and NC-CNT-1000, respectively.

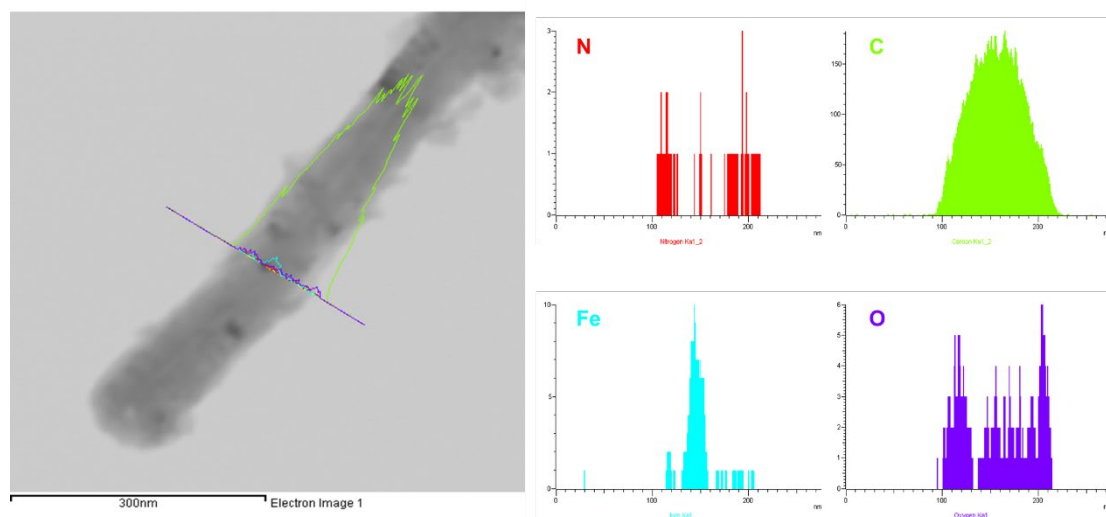


Figure S6 TEM image of the NC-CNT-1000 and its corresponding line profile concentration for N, C, Fe and O. The intensive distribution of N, O on the edge, and the peak distribution of Fe and C on center axis of the tubular structure was resulted from the N-doped carbon coating layer on surface of the MWCNTs, and the residual Fe particle in the MWCNTs, respectively.

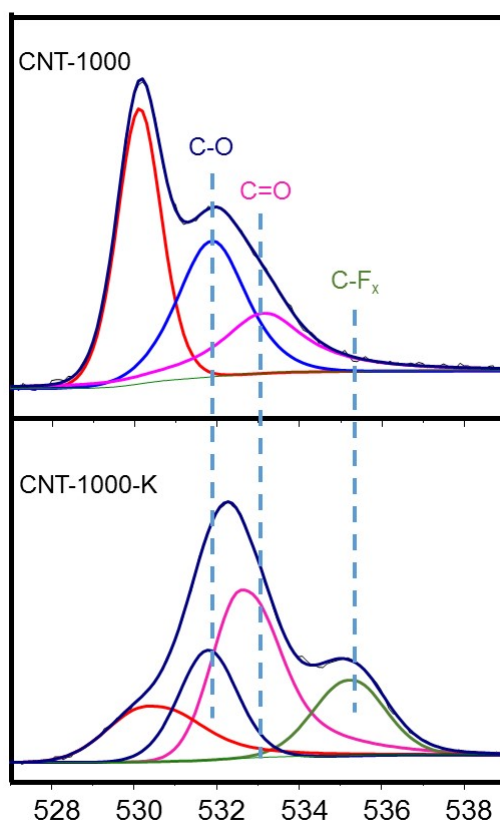


Figure S7 The XPS O 1s spectra of (a) CNT-1000 and (b) CNT-1000-K. The CNT-1000-K refers to the sample obtained after the stability test. The increased ratio of C=O bond in CNT-1000 after current-time chronoamperometric test proved the additional connection of oxygen-contained functional groups on the surface of CNT-1000 during the electrochemistry process.

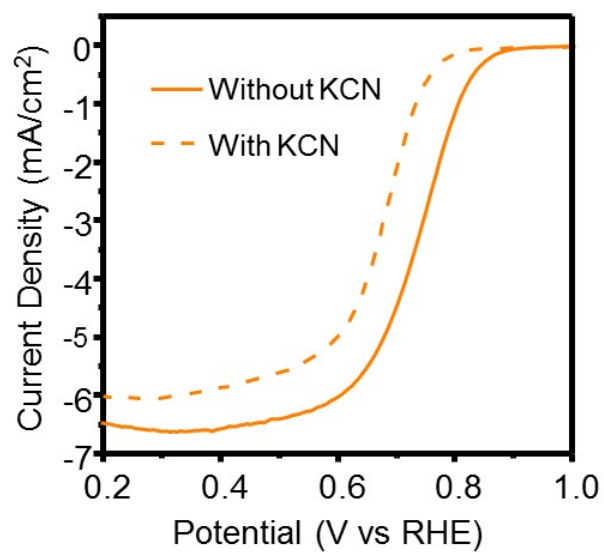


Figure S8 Linear sweep voltammetry (LSV) of NC-CNT-1000 at 10 mV s^{-1} in the presence of oxygen at 1600 rpm in 0.1 M KOH with and without cyanide ions (10 mM KCN). The reduction of saturated current density and half-wave potential with existing KCN illustrated the contribution of Fe-derived active sites to the ORR activity of the sample.

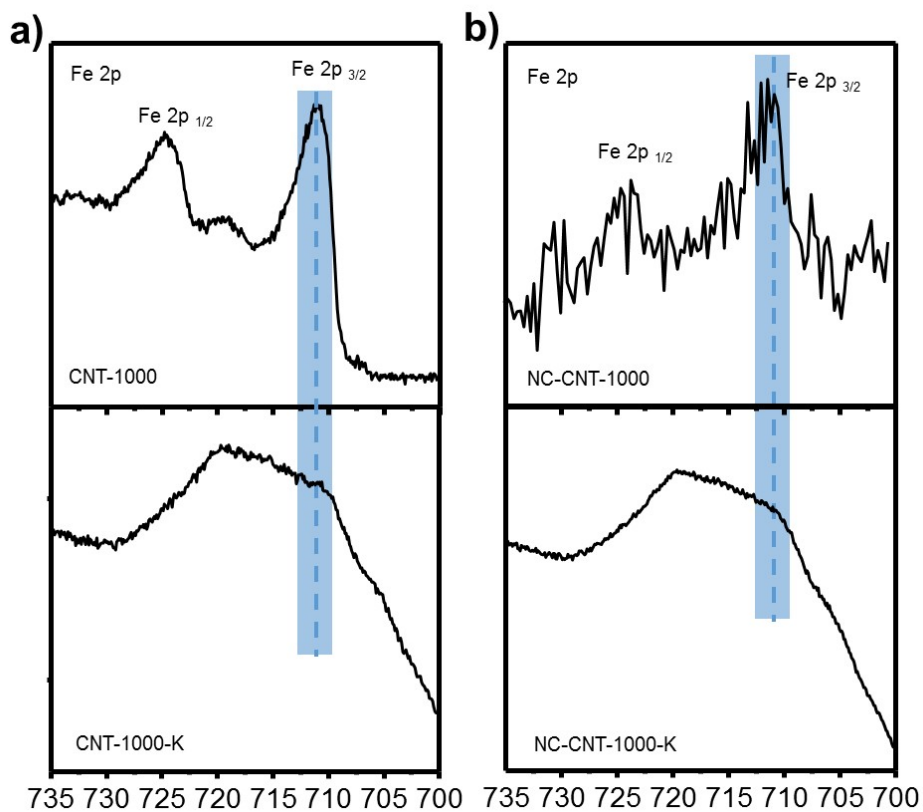


Figure S9 the high-resolution Fe 2p spectra of (a) CNT-1000 and (b) NC-CNT-1000 before and after long term stability test in 0.1 M KOH. The CNT-1000-K and NC-CNT-1000-K refers to the sample obtained after the stability test. Visibly negative shift of Fe 2p $_{3/2}$ peak can be observed in CNT-1000-K, which was due to the change of chemical environment of Fe, most probably derived from the degradation of active sites.

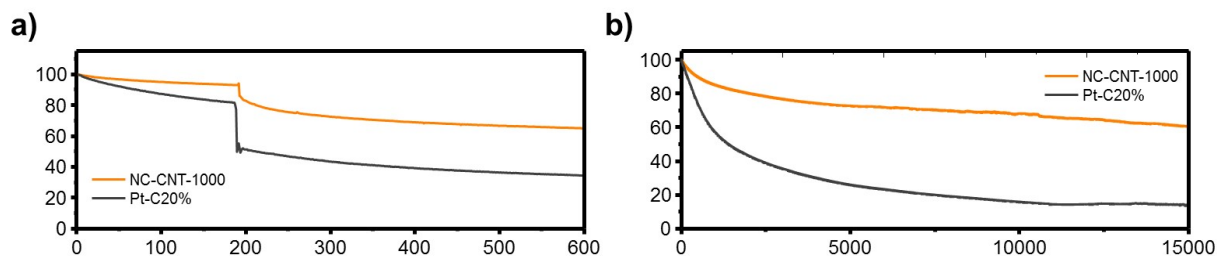


Figure S10 Chronoamperometric response of samples: (a) tolerance against methanol and (b) long-term stability in 0.1 M HClO₄. The NC-CNT-1000 demonstrated better tolerance towards MeOH poison and superior long-term stability compared with commercial Pt-C catalysts.

Table S1 Mass record of the samples during synthesis process.

	Precursor (mg)	After HTC (mg)	After Annealing (mg)
CNT+NC	408	163	98
NC	360	115 ^a	50 ^a
CNT	48	48 ^b	48 ^b

^a The mass is estimated by subtract the mass of CNT from that of CNT+NC.

^b The mass is estimated due to the inert property of CNT, we assume that the mass of CNT does not change during the reaction.

Table S2 Summary of specific surface area and pore volume of different samples based on N₂ adsorption measurement at -196 °C.

Sample	CNT-1000	CS-CNT-1000	CS-1000
SSA (m ² g ⁻¹)	36	187	523
Pore volume (cm ³ g ⁻¹)	0.11	0.19	0.49
Micropore volume (cm ³ g ⁻¹)	0	0.06	0.16

Table S3 Summary of XPS survey spectra of different samples.

Sample	Atom Species (at. %)					
	C	O	N	Fe	N/C	Fe/C
CNT-1000	98.08	1.84	0	0.08	0	0.0008
NC-CNT-1000	93.61	5.15	1.20	0.04	0.01	0.0004

Table S4 Summary of XPS N1s spectra from Fig. S4

Sample	N Species (at. %)			
	Pyridinic-N	Fe-N _x	Graphitic-N	Oxidized-N
NC-CNT-1000	18.26	10.96	57.16	13.62