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SUPPLEMENTARY INFORMATION

Scalable Synthesis of Bi-functional High-Performance Carbon Nanotube Sponge Catalysts and Electrodes with Optimum C-N-Fe Coordination for Oxygen Reduction Reaction

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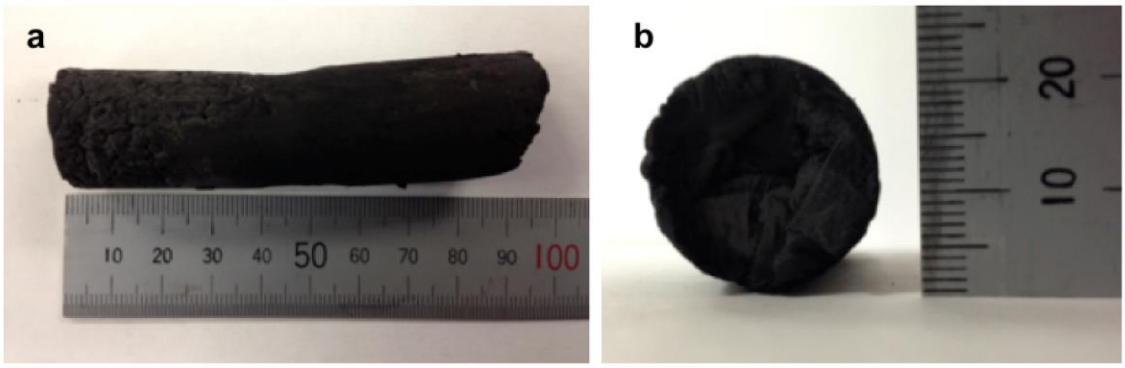

Fig. S1: a,**b** Photos of an as-synthesized cylindrical CNT sponge.

Table S1 Cost Analysis and Comparison of CNT sponge synthesis methods

	This work (30 min growth)		**Literature (240 min growth)**	
	Amount	Cost	Amount	Cost
Ferrocene, 98% ($108 for 500 g) *	0.3 g	$ 0.065	1.87 g (0.06 g/mL × 0.13 mL/min × 240 min)	$0.404
1,2-Dichlorobenzene, 99% ($169 for 2 L) *	-	-	31.2 mL (0.13 mL/min × 240 min)	$2.636
C_2H_4, UHP ($22 for/300 ft^3) **	2.4 L (80 sccm × 30 min)	$ 0.064	-	-
H_2, UHP ($45 for 300 ft^3) **	7.8 L (260 sccm × 30 min)	$ 0.041	72 L (300 sccm × 240 min)	$0.381
Ar, UHP ($48 for 300 ft^3) **	2.4 L (80 sccm × 30 min)	$ 0.014	480 L (2000 sccm × 240 min)	$2.712
Yield / Total cost	1.8 g 2.2 cm (diameter), 10 cm (length)	$ 0.184	0.072 g 4 cm (length), 3 cm (width), 0.8 cm (thickness)	$6.133
Production rate / Normalized cost	3.6 g/h 76 cm^3/h	$ 0.1/g	0.018 g/h 2.4 cm^3/h	$85.2/g

* Price information was obtained from Sigma-Aldrich website at the time the manuscript was prepared.

** Price information was quoted from Airgas at the time the manuscript was prepared.

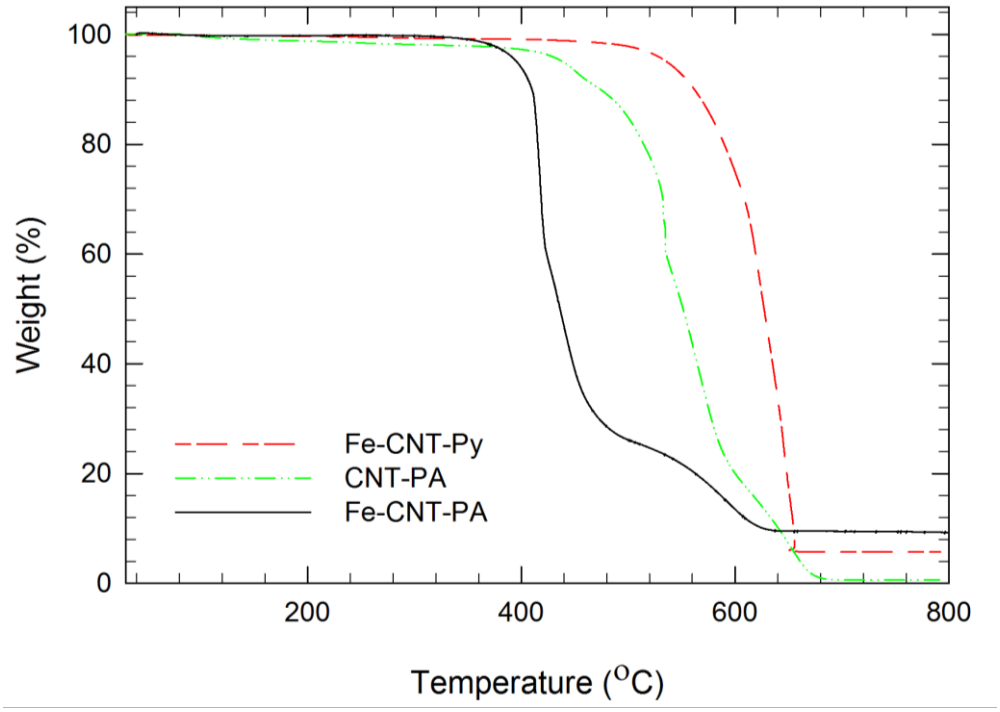

Fig. S2: TGA results of Fe-CNT-Py (red), CNT-PA (green), and Fe-CNT-PA (black).

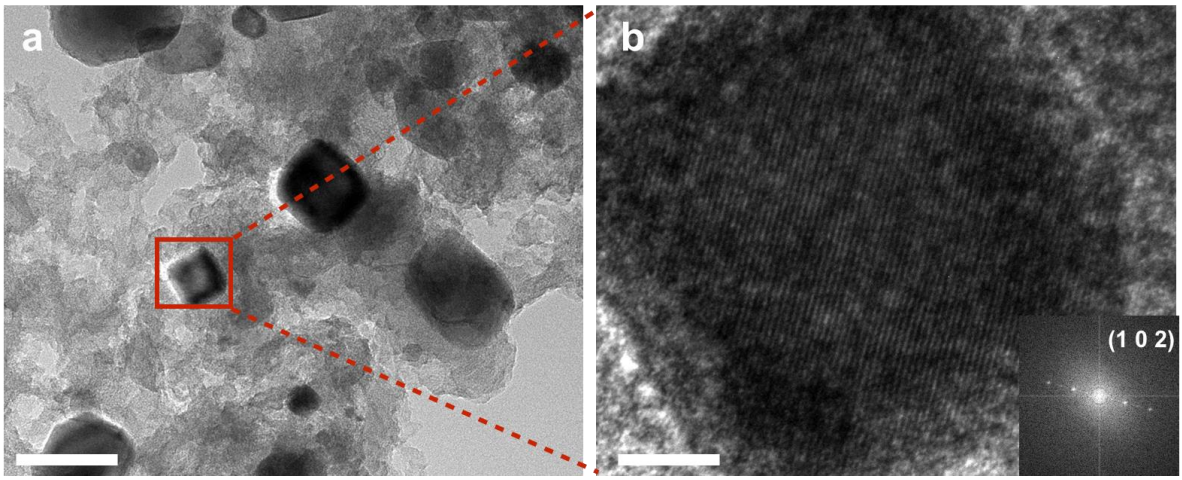

Fig. S3: HRTEM images of the aggregated portion in Fe-CNT-PA (see Fig. 2d). The inset shows the fast Fourier transform pattern. The scale bars indicate 100 nm for **a** and 10 nm for **b**.

The effect of nitrogen doping was also studied by Raman spectroscopy. The two peaks at ~1330 cm^{-1} and ~1580 cm^{-1} in Fig. S3a can be assigned to D-band and G-band, respectively. The G-band presents graphitic structure while the D-band indicates defects due to disordered graphitic carbon[2]. The intensity ratios of D-band to G-band (I_D/I_G) can be considered as one of the key parameters to indicate the defect level in CNTs. By comparing the I_D/I_G and the nitrogen at%, we found that I_D/I_G was increased with nitrogen at% presumably due to disorder or defects in the graphitic carbon structure with the nitrogen substitution. In addition, broader D-band and G-band peaks were observed with higher nitrogen at%, which may suggest the disorder in the basal plane of graphitic carbon layers[2, 3]. The shift of the G-bands of the nitrogen-doped samples towards higher frequencies compared to Fe-CNT could be explained by the stronger C-N bonding compared with C-C bonding[3].

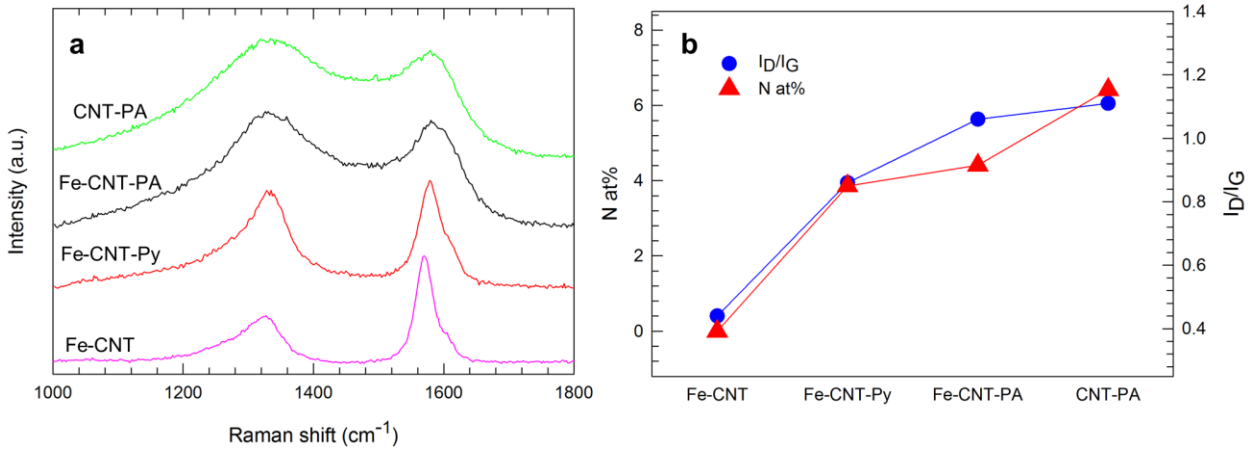

Fig. S4: a, Raman spectra of Fe-CNT (pink), Fe-CNT-Py (red), Fe-CNT-PA (black), and CNT-PA (green). **b,** nitrogen at% and I_D/I_G of Fe-CNT, Fe-CNT-Py, Fe-CNT-PA, and CNT-PA.

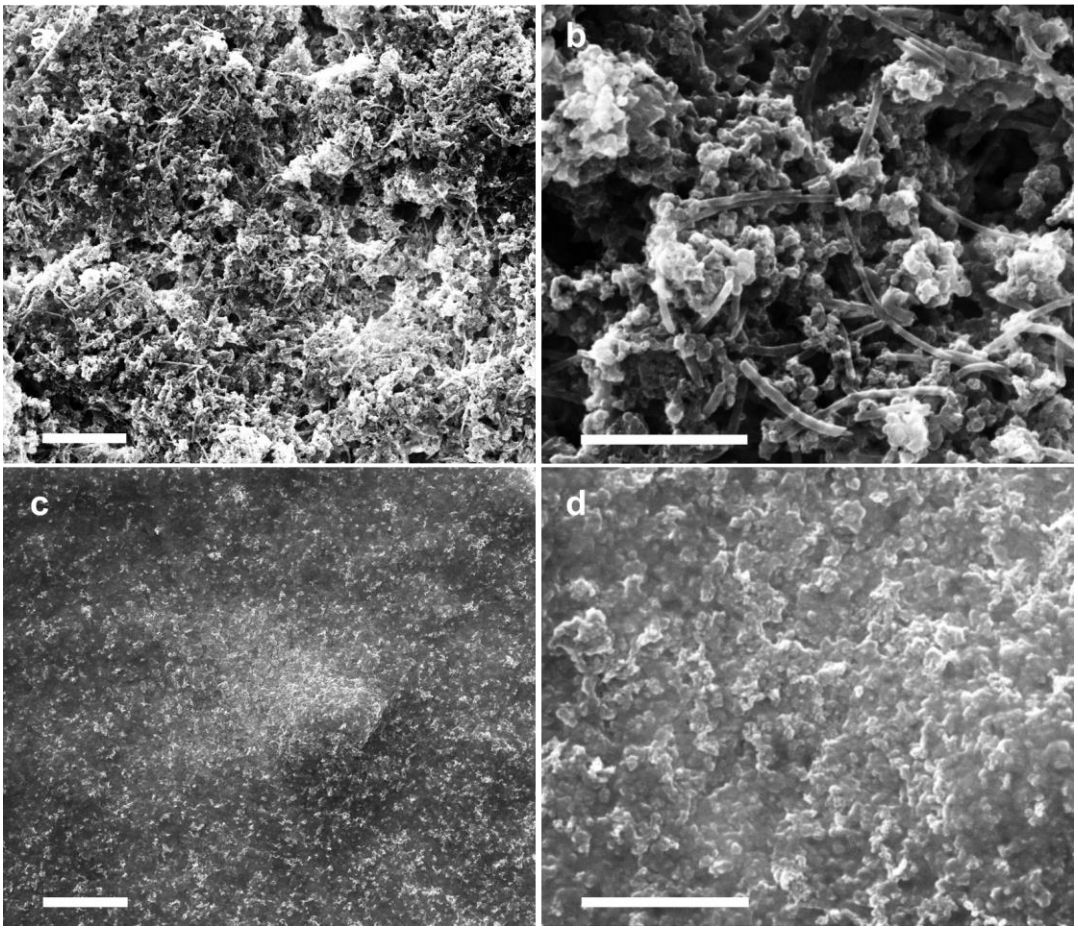

Fig. S5: SEM images of the catalyst ink made of Fe-CNT-PA (a,b) and Pt/C (c,d). The ink was dopped and dried on copper foils for taking the SEM images. The scale bars indicate 10 μm for (a,c) and 4 μm for (b,d).

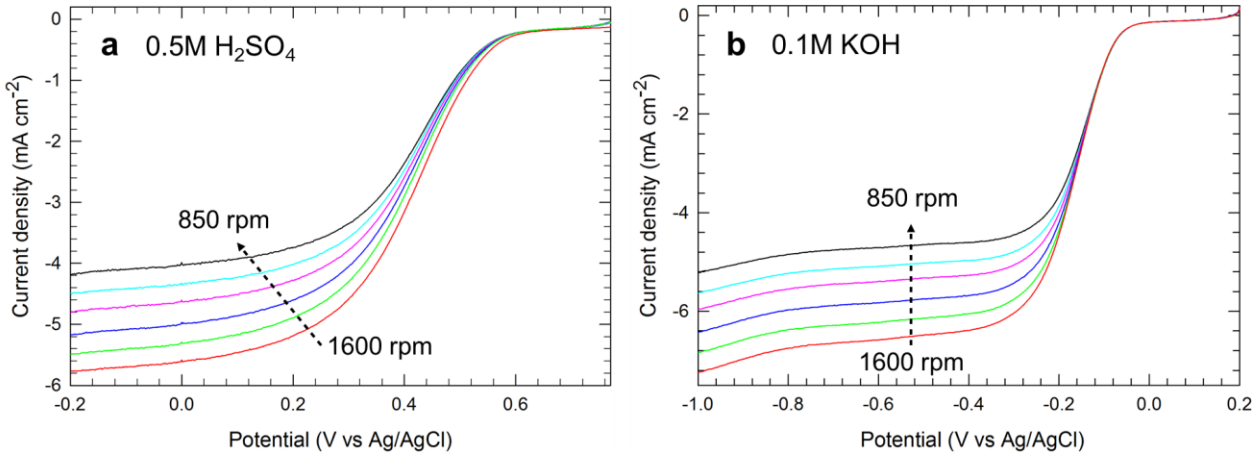

Fig. S6: RDE test results at 1600 rpm and lower rotating speeds (every 150 rpm) with Fe-CNT-PA in O_2-saturated 0.5M H_2SO_4 for **a** and O_2-saturated 0.1M KOH for **b**.

The atomic compositions and XPS results of the nitrogen doped samples are additionally provided in Table S2 and Fig. S7.

Table S2. Atomic composition of the nitrogen-doped samples

	C at%	N at%	O at%	S at%	Fe at%
CNT-PA	89.57	6.42	3.70	0.22	0.09
Fe-CNT-Py	93.34	3.86	1.90	0.00	0.90
Fe-CNT-PA	88.80	4.41	4.30	1.01	1.48

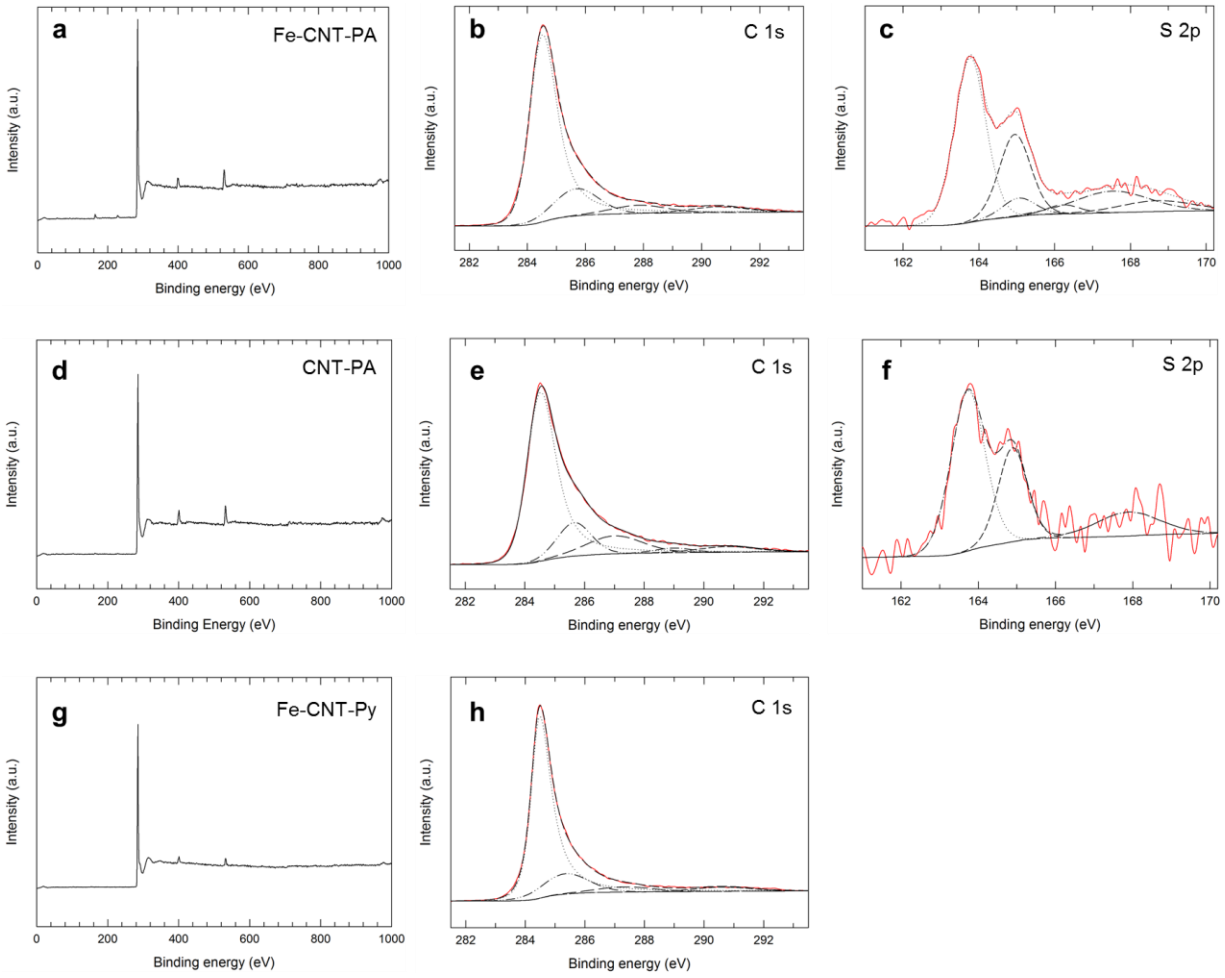

Fig. S7: XPS spectra of Fe-CNT-PA (a,b,c), CNT-PA (d,e,f), and Fe-CNT-Py (g,h). The left column (a,d,g) shows survey scans; the middle column (b,e,h) shows high resolution scans of C 1s; and the right column (c,f) shows high resolution scans of S 2p.

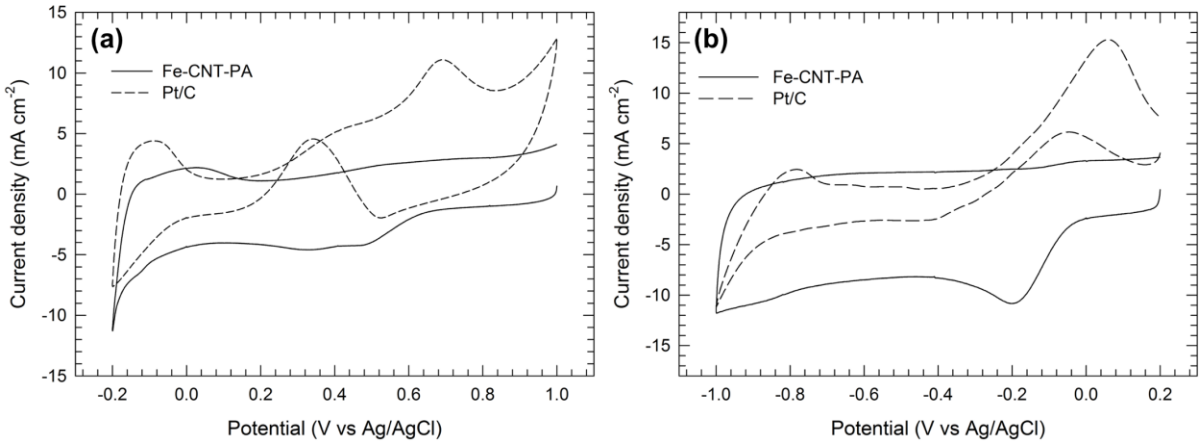

Fig. S8: CV tests of Fe-CNT-PA and Pt/C in O_2-saturated 0.5M H_2SO_4 (a) and 0.1M KOH (b) in the presence of 1.0 M methanol.

Specific surface area is an important factor for ORR catalysts, so we carried out Brunauer–Emmett–Teller (BET) tests (Micrometrics ASAP 2020 physisorption analyzer) as well as theoretically calculated the specific surface area of our CNT sponge with the following relation.[1]

$$Specific\ surface\ area = \frac{1315 d_e}{n d_e - 0.68\left[\sum_{i=1}^{n-1} i\right]}$$

where d_e is the external diameter of CNTs (122 ~ 131 nm from Fig. 2b,e) and n is the number of shells in an individual CNT which can be calculated by dividing the shell thickness with the interlayer distance (0.34 nm) of graphitic layers. The shell thickness is the half of the difference between external diameter and the inner diameter (24 ~ 50 nm) of the tube. The BET test showed the specific surface area of our pristine CNT sponge was found to be ~11 m^2/g, which is close to calculation results of 14 ~ 18 m^2/g.

References

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2. Dresselhaus, M. S.; Jorio, A.; Saito, R. *Annu. Rev. Condens. Matter Phys.* **2010,** 1, (1), 89-108.
3. Kundu, S.; Nagaiah, T. C.; Xia, W.; Wang, Y. M.; Van Dommele, S.; Bitter, J. H.; Santa, M.; Grundmeier, G.; Bron, M.; Schuhmann, W.; Muhler, M. *J. Phys. Chem. C* **2009,** 113, (32), 14302-14310.