Supporting Information

Ideal N-doped carbon nanoarchitectures evolved from fibrils for highly efficient oxygen reduction

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The crystallite size (D) of the planes corresponding to C (100) and (002) diffraction peaks were estimated by using the Scherrer equation as follows[S1]. The calculated values were 1.7~2.8 nm and 0.8~1.0 nm, respectively. The average number of graphitic stacked layers in the catalytic materials was calculated by dividing the interplanar spacing of (002) (~0.35 nm).

$$D = \frac{K\lambda}{\beta\cos\theta} \qquad (1)$$

where λ denotes the wavelength of X-ray (1.5418 Å), θ is the diffraction angle of the corresponding peak, β is half-peak width and K equals to 0.89.

The overall electron transfer numbers per oxygen molecule involved in a typical ORR process were calculated from the slopes of the Koutecky-Levich (K-L) plots using the following equations:[S2,S3]

$$J^{-1} = (J_L)^{-1} + (J_K)^{-1} = (B\omega^{0.5})^{-1} + (J_K)^{-1} \qquad (2)$$

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

Where J is the measured current; J_L and J_K are the diffusion- and kinetic- limiting currents, respectively; B is the reciprocal of the slope; ω is the electrode rotating speed in rpm; n is the electron transfer numbers per oxygen molecule; F is the Faraday constant (96485 C mol^{-1}); C_0 is the concentration of O_2; D_0 is the diffusion coefficient of O_2 and ν is the kinematic viscosity of the electrolyte. C_0, D_0 and ν are 1.2 × 10^{-3} M, 1.9 × 10^{-5} cm^{-5} s^{-1}, and 0.01 cm^2 s^{-1} for O_2-saturated 0.1 M KOH, respectively, in this study.

Supporting information for evaluating the cost of the NACC or NFTC sample:

Preparing 1 kg NACC or NFTC needs: (price is based on U.S. dollar)

Ammonia: $ 390.0 (80 sccm × 60 min × 12 h / 1000 ml L^{-1} / 22.4 L mol^{-1} × 17 g mol^{-1} × $ 9.0 kg^{-1})

Absorbent cotton or facial tissue: about $ 50.0

Electric charge: less than $ 400.0

Therefore, it takes less than $ 1000.0 for the raw-materials and electricity to prepare 1 kg catalytic material. 1 kg 20 wt.% Pt/C needs about $70 000.0 (Fuel cell store, http://www.fuelcellstore.com/en/pc/viewCategories.asp?idCategory=79), it is over 50 times higher than the cost of preparing 1 kg NACC or NFTC. Considering that entire preparation process is quite simple, these novel materials exhibit huge competitive advantage in total cost compared to the commercial Pt/C catalyst.

Reference for supporting information:

[S1] M. Zhong, E. K. Kim, J. P. McGann, S. E. Chun, J. F. Whitacre, M. Jaroniec, K. Matyjaszewski, T. Kowalewski. *J. Am. Chem. Soc*. **2012**, *134,* 14846.

[S2] Y. Liang, Y. Li , H. Wang, J. Zhou, J. Wang, T. Regier, H. J. Dai. *Nat. Mater.* **2011**, *10,* 780.

[S3] U. A. Paulus, T. J. Schmidt, H. A. Gasteiger, R. J. Behm. *J. Electroanal. Chem.* **2001**, *495,* 134.

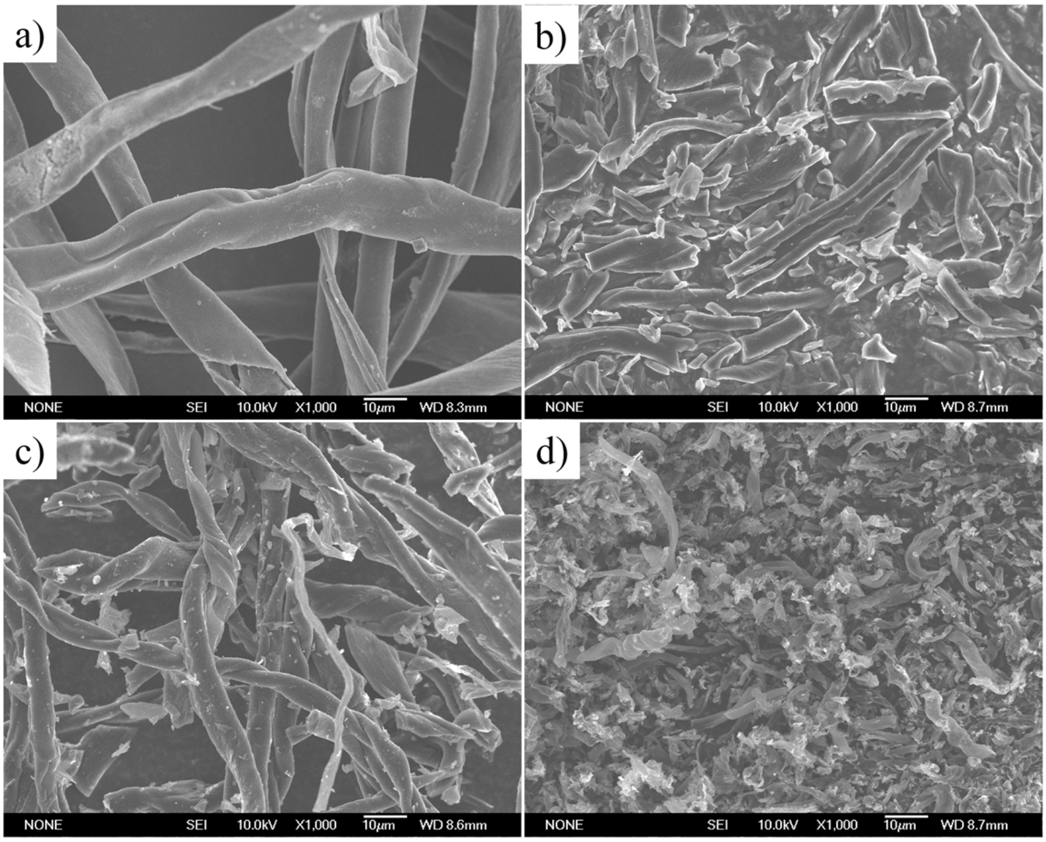

Figure S1. Typical scanning electron microscopy (SEM) images of a) absorbent cotton, b) NACC-650, c) NACC-800 and d) NACC-1050.

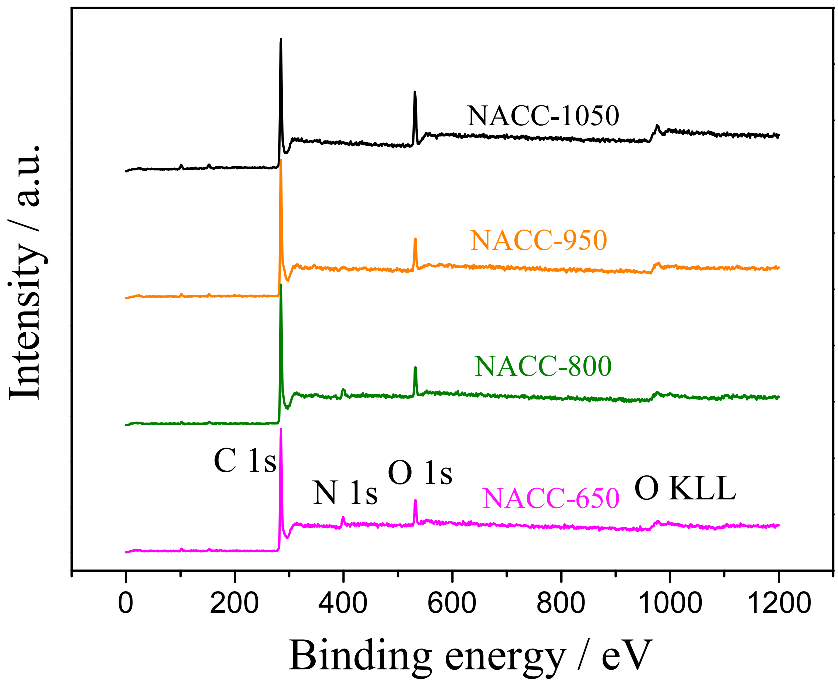

Figure S2. XPS spectra of the NACC materials

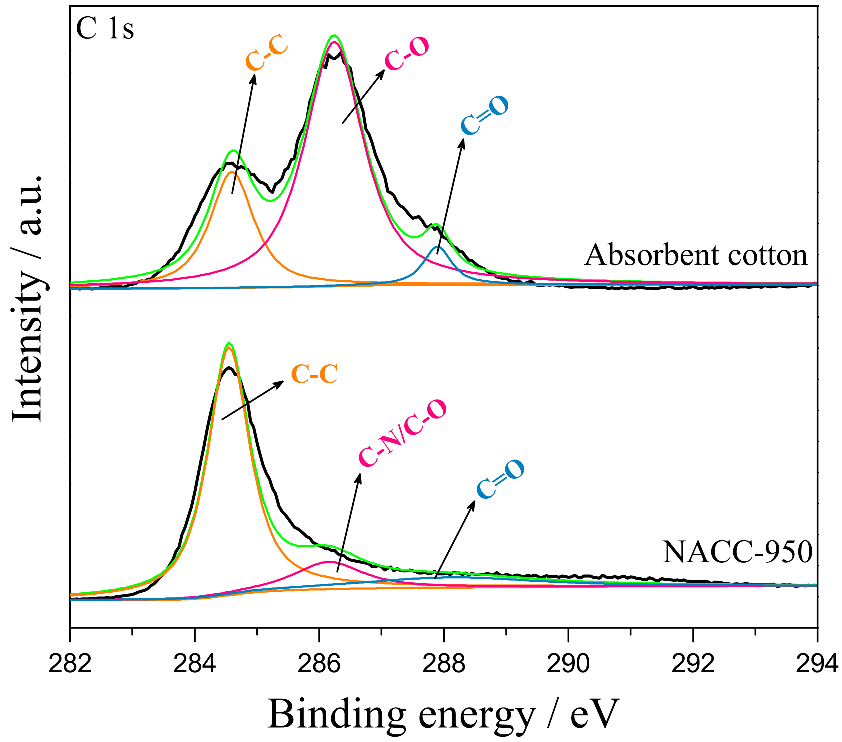

Figure S3. High resolution C 1s XPS spectra of absorbent cotton and NACC-950.

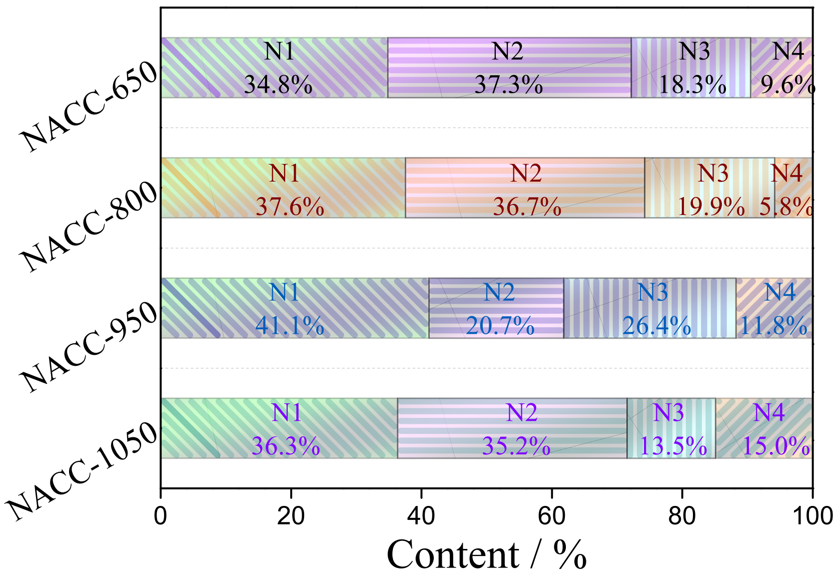

Figure S4. Relative ratios of the deconvoluted peak areas of N 1s XPS spectra.

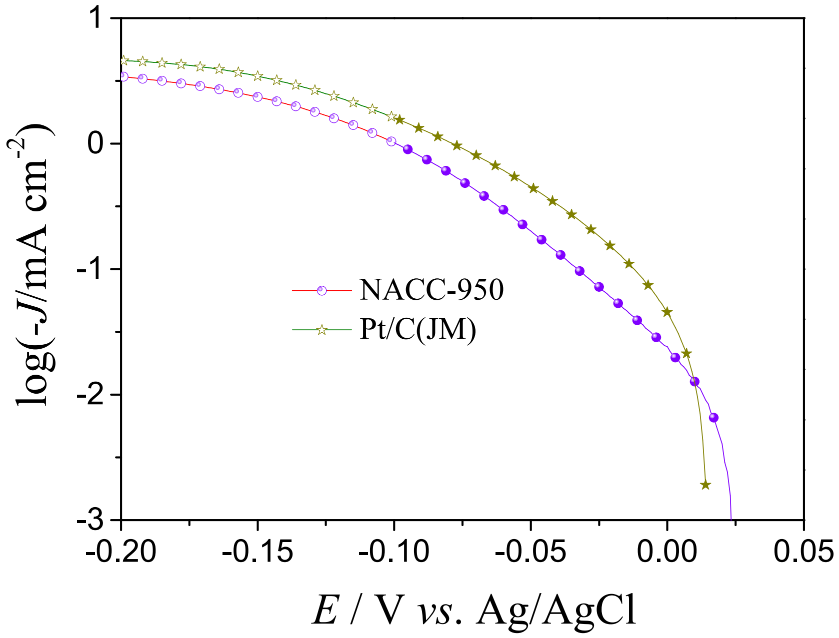

Figure S5. Diffusion-corrected Tafel plots for ORR on NACC-950 and Pt/C. Catalyst loading was 0.10 mg cm^{-2}.

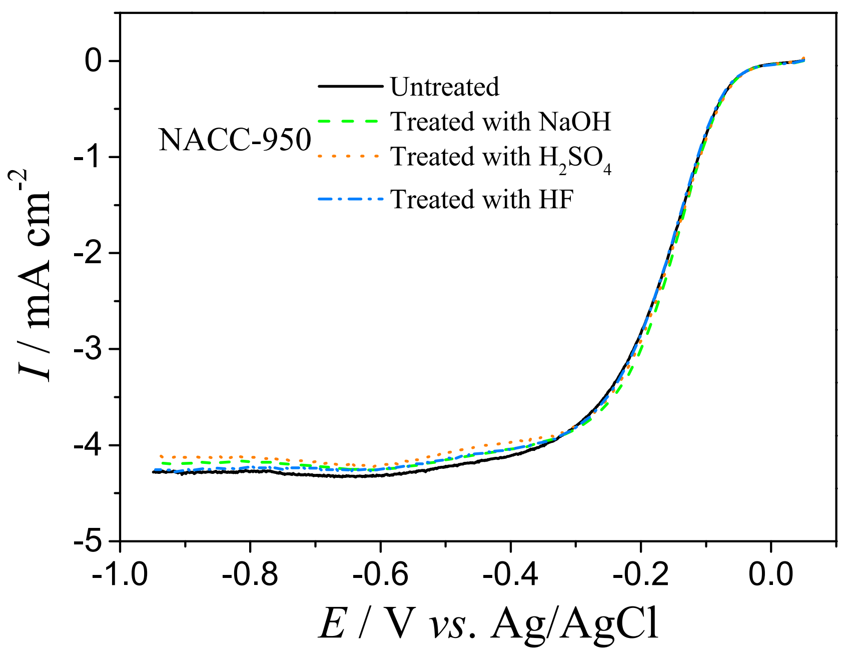

Figure S6. Rotating-disk voltammograms of NACC-950 with or without acid/alkali treatment at the sweep rate of 5 mV s^{-1} in O_2-saturated 0.1 M KOH. Catalyst loading for all samples was 0.10 mg cm^{-2}.

Table S1. Comparison of electrochemical performance of commercial Pt/C and the prepared catalytic materials.

	Pt/C	NACC -1050	NACC -950	NACC -800	NACC -650	NACC -950	NFTC	NFPC	NAPC
Catalyst loading (mg cm^{-2})	0.10	0.10	0.10	0.10	0.10	0.30	0.30	0.30	0.30
Coulombic charge between -0.8 and 0.4 V of the dash lines in Figure 4a (mC)	4.55	1.92	3.59	4.58	0.24	—	—	—	—
Onset potential in LSV (E_{onset}, V)	0.00	-0.06	-0.01	-0.10	-0.27	0.00	0.00	0.00	-0.03
Half-wave potential in LSV ($E_{1/2}$, V)	-0.12	-0.17	-0.13	-0.25	-0.38	-0.12	-0.12	-0.13	-0.18
Current at -0.2 V in LSV (mA cm^{-2})	4.65	2.37	3.46	0.48	0.01	4.13	4.11	3.42	1.50
Limiting current at -0.95 V in LSV (mA cm^{-2})	5.03	4.09	4.42	3.03	2.46	5.09	5.73	5.26	3.64
Electron transfer number (n) at -0.6 V in LSV	3.98	3.49	3.81	2.84	2.13	—	—	—	—

Table S2. Comparison of ORR performance of some N-doped carbon materials in literature.

Source/References	Solution	Loading (mg cm^{-2})	Activity (V vs. Ag/AgCl)
In this work (NACC-950)	0.1 M KOH	0.30	E_{onset} = 0.00 $E_{1/2}$ = -0.12
Angew. Chem. Int. Ed. 2014, 53, 1570–1574 **(N-doped carbon nanosheets)**	0.1 M KOH	0.60	E_{onset} = -0.01 $E_{1/2}$ = -0.13
J. Am. Chem. Soc., 2011, 133, 206–209 **(Mesporous N-doped carbon)**	0.1 M KOH	0.66	E_{onset} = -0.0035
Adv. Mater. 2013, 25, 998–1003 **(N-doped carbon spheres)**	0.1 M KOH	Not mentioned	E_{onset} = 0.00 $E_{1/2}$ = -0.10
Adv. Mater. 2013, 25, 6226–6231 **(N-doped Graphene/Ordered Porous Carbon)**	0.1 M KOH	0.42	E_{onset} = -0.05

Table S3. Content of metallic impurities in NACC-950 as determined by ICP-OES analysis.

Impurity	Content (wt.%)
Co	0.0002
Fe	0.0252
Mn	0.0007
Ni	0.0015