

Supporting Information

**Enhancement of Nitrogen Self-Doped Nanocarbons
Electrocatalyst Activity *via* Tune-up Solution Plasma**

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Characterization of plasma

To observe the electrical properties of the solution plasma (SP), the current-voltage (I-V) waveforms were measured using oscilloscope (DLM 2024, Yokogawa) with a current probe (PBC 50 and PBC 100, 50 and 100 MHz, respectively, Yokogawa) and a differential high-voltage probe (PBDH 0150, 150 MHz, Yokogawa). Also, to analyze the optical properties of SP, the optical emission spectrum (OES) during discharge was recorded by a spectrograph (USB 4000, Ocean Optics) with an integration time of 100 ms. The optical fiber (P400-2-UV/VIS, Ocean) was fixed in a quartz tube above the discharge.

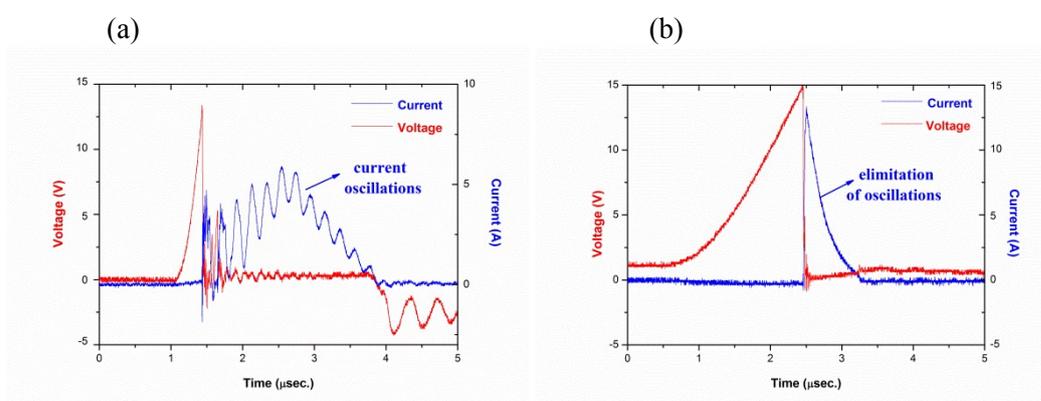


Fig. S1 Current-voltage waveforms of SP discharge with (a) conventional, and (b) tune-up SP. The voltage (left graph) and the current (right graph) waveforms of the plasma in pyridine. The current oscillations were successfully eliminated after tune-up SP.

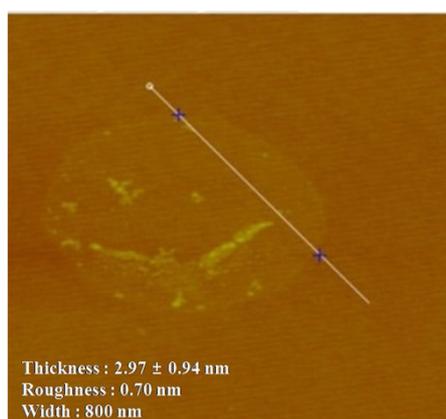


Fig. S2 AFM image of nitrogen doped graphitic carbon nanosheets (NGS).

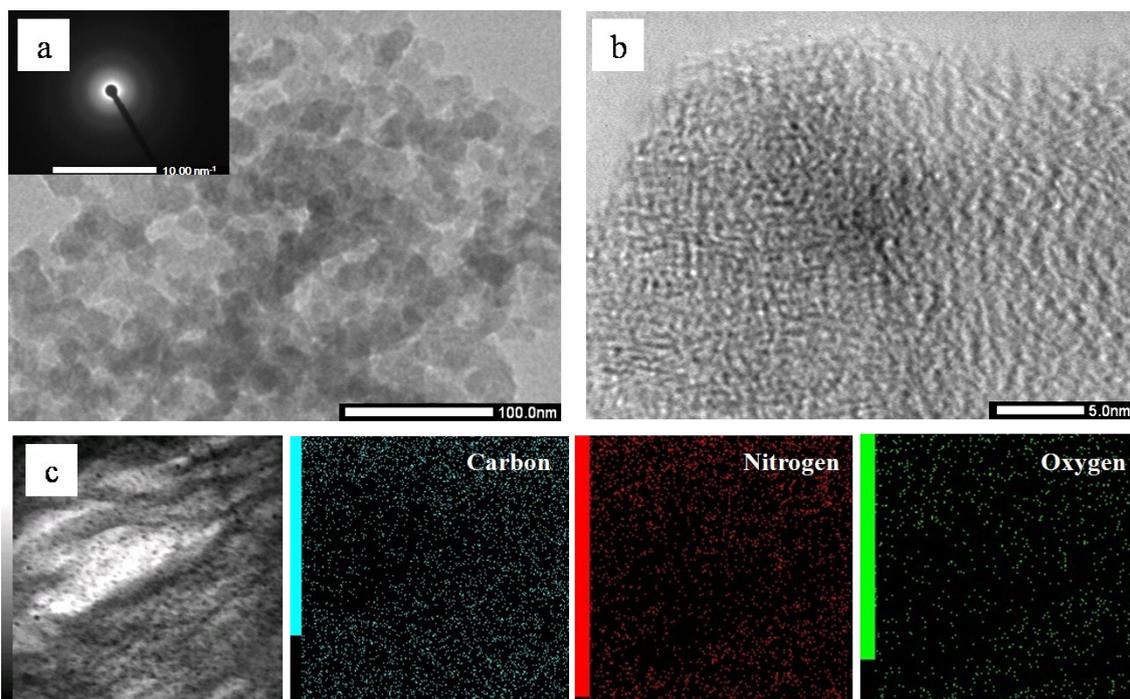


Fig.S3 (a) Wide-field TEM images of NAP; the corresponding SAED pattern (inset) shows a broad ring-like pattern without any diffraction spots, suggesting the amorphous phase. (b) HR-TEM images of NAP. (c) Dark-field TEM image of NAP, and the corresponding carbon, nitrogen, and oxygen element mapping images.

Table S1 Textural parameters derived from the N_2 adsorption-desorption isotherms of NAG and NAP.

Samples	Shape	Surface area (m^2/g)	Pore volume (cm^3/g)	Mean pore diameter (nm)
NGS	Sheet-like	621.48	1.54	4.96
NAP	Sphere-like	48.09	0.12	10.24

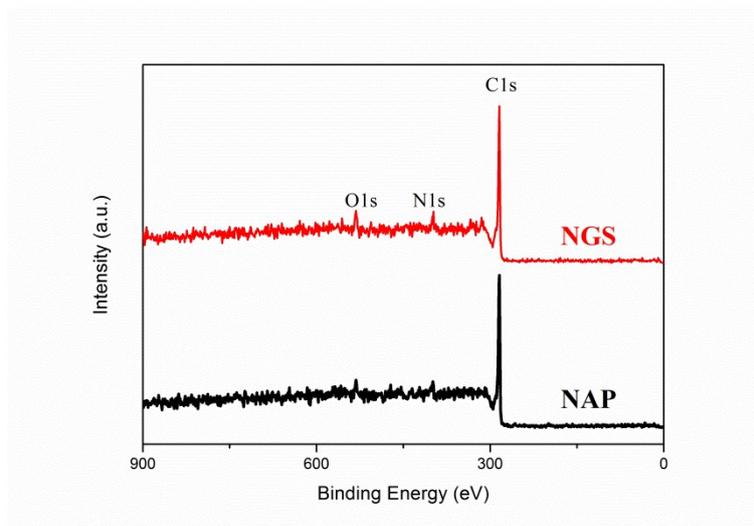


Fig. S4 XPS spectra of NGS and NAP. The XPS spectra of all samples shows the major peaks corresponding to C 1s, N 1s and O 1s, while a significant peak from tungsten was not detected during any measurements. This suggests that the erosion of tungsten electrode during SP discharge is negligible. In addition, the spectra show the presence of very small amount of surface adsorbed oxygen.

Table S2 Surface elemental compositions in NGS and NAP by XPS analysis.

(at. %)	C	O	N	N/C
NGS	88.80	5.20	6.00	0.05
NAP	90.80	6.10	2.90	0.02

Table S3 Bulk elemental compositions in NGS and NAP by elemental analysis (EA).

(wt. %)	C	H	N	N/C
NGS	85.17	5.82	2.55	0.05
NAP	89.31	1.24	0.96	0.01

The XPS data give that the nitrogen content of NGS (6.0 at.%) was around two times higher than that of NAP (2.9 at.%), which was almost similar to the results acquired from EA analysis. This can be regarded that the surface is enriched with nitrogen atoms because the graphitic sheets stacks are thicker than the information depth. Also, a non-uniform distribution of surface groups throughout the carbon sample may explain this observation.⁵⁹

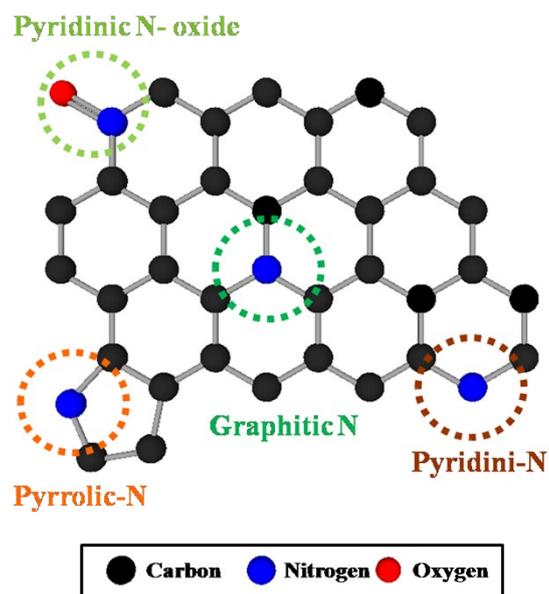


Fig. S5 Schematic of four types of N atoms in the nitrogen self-doped nanocarbons; pyridinc-N and pyrrolic-N is located on the edge of the graphite matrix and graphitic-N can be both edge-graphitic N and bulk-like grphitic-N.

Table S4 Total surface nitrogen content and concentration of different nitrogen functionalities acquired by XPS

Samples	Nitrogen Content (at%)	Concentration of different nitrogen functionalities (at%)			
		Pyridinic-N	Pyrrolic-N	Graphtic-N	N-oxides of pyridinic-N
NGS	6.0	3.3	1.3	1.2	0.2
NAP	2.9	1.4	0.2	1.1	0.2

Table S5 The conductivity test results of all samples and references.

Samples	Resistivity ρ ($\Omega\cdot\text{cm}$)	Conductivity (S cm^{-1})	Ref
NGS	0.042	23.80	This work
NAP	1.4	0.71	This work
B and N doped graphitic carbon nanosheets	0.0289	34.60	[S1]
Nitrogen-doped CNTs	0.04	25	[S2]

Table S6 The ORR activity of N-doped carbon materials depends on different synthesis methods.

	Synthesis method	n	Ref
N-doped graphene	Wet chemical reaction	2.6	[S3]
N-doped CNT	CVD	3.5	[S4]
N-doped OMCs	Thermal treatment	3.4	[S5]
NGS (This work)	Solution plasma	3.8	This work

Koutecky–Levich (K–L) analysis ⁶⁴

$$1/j = 1/j_L + 1/j_k \quad (1)$$

$$1/j = 1/B\omega^{1/2} + 1/j_k \quad (2)$$

$$B = 0.201 n F A C_{O_2} D_0^{2/3} \nu^{-1/6} \omega^{1/2} \quad (3)$$

where, j is the measured current density (mA/cm^2), j_k and j_L are the kinetic and diffusion-limiting current densities (mA/cm^2), ω is the angular velocity of the disk in rpm, F is the Faradays constant ($F= 96485 \text{ C mol}^{-1}$), n is the number of electrons transferred per oxygen molecule, $C_{O_2}^*$ and D_0 are the oxygen bulk concentration ($1.2 \times 10^{-3} \text{ mol cm}^{-3}$) and diffusion coefficient of O_2 ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), respectively, and ν is the kinematic viscosity of the electrolyte ($1.1 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$).

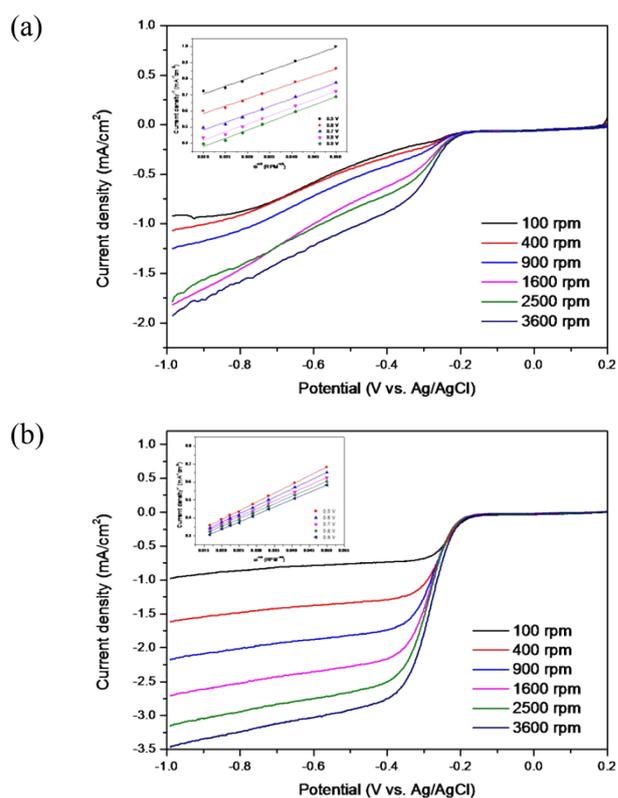


Fig. S6 (a) LSV curves of NAP electrode in O₂-saturated 0.1 M KOH solution with a sweep rate of 10 mV s⁻¹ at the different rotation rates. (inset) Corresponding Koutecky-Levich (K-L) plots at different potentials. (b) LSV curves of NGS electrode in O₂-saturated 0.1 M KOH solution with a sweep rate of 10 mV s⁻¹ at the different rotation rates. (inset) Corresponding Koutecky-Levich (K-L) plots at different potentials.

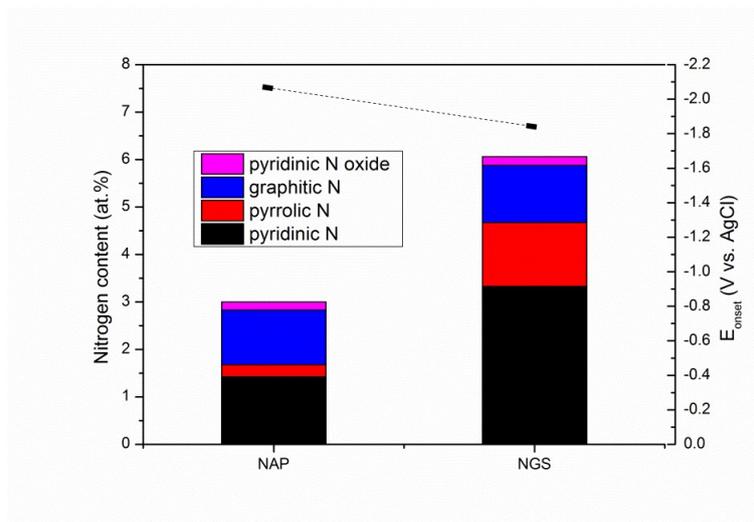
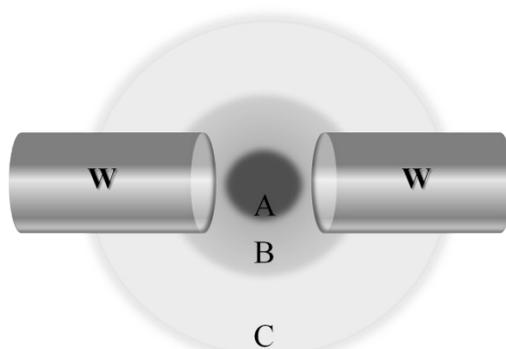


Fig. S7 The dependence of onset potential on the N functionality distribution.



A: Plasma, 5000 K
 B: Interface of Plasma/Gas
 C: Interface of Gas/Liquid, 350 K

Fig. S8 Reaction areas according to temperature distributions during the synthesis of NAP.

Reference

- S1. K. Fujisawa, T. Tojo, H. Muramatsu, A. L. Elías, S. M. Vega-Díaz, F. Tristán-López, J. H. Kim, T. Hayashi, Y. A. Kim, M. Endo and M. Terrones, *Nanoscale*, 2011, **3**, 4359.
- S2. L. Wang, P. Yu, L. Zhao, C. Tian, D. Zhao, W. Zhou, J. Yin, R. Wang and H. Fu, *Sci. Rep.*, 2014, **4**, 5184.
- S3. Y. Zhang, K. Fugane, T. Mori, L. Niu and J. Ye, *J. Mater. Chem.*, 2012, **22**, 6575.
- S4. Y. Ma, L. Sun, W. Huang, L. Zhang, J. Zhao, Q. Fan and W. Huang, *J. Phys. Chem. C*, 2011, **115**, 24592.
- S5. X. Wang, J. S. Lee, Q. Zhu, J. Liu, Y. Wang and S. Dai, *Chem. Mater.*, 2010, **22**, 2178.