Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Solution Plasma Synthesis of Boron-Carbon-Nitrogen Catalyst with Controllable Bond Structure

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Koutecky–Levich (K–L) analysis [43]

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

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

$$B = 0.201\ n\ F A\ C_{O2} D_o^{2/3}\ \nu^{-1/6} \qquad \omega^{1/2} \quad (3)$$

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 C mol^{-1}), n is the number of electrons transferred per oxygen molecule, C_o * and D_o are the oxygen bulk concentration (1.2 x10^{-3} mol cm^{-3}) and diffusion coefficient of O_2 (1.9 X 10^{-5} cm^2 s^{-1}), respectively, and ν is the kinematic viscosity of the electrolyte (1.1 × 10^{-2} cm^2 s^{-1}).

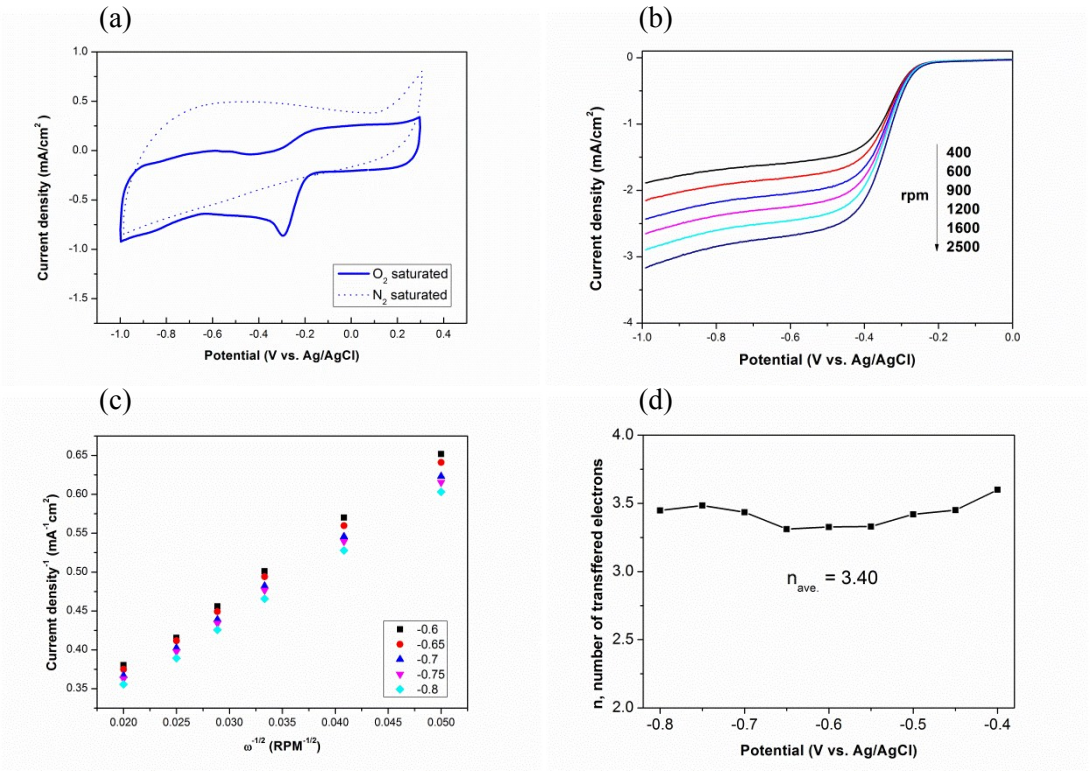

Fig. S1 Electrochemical measurements of B/N uncoupling: (a) CV curves of the ORR in O_2 and N_2-saturated 0.1M KOH solutions at a scan rate of 10 mV s^{-1}. (b) LSV curves of the ORR in O_2-saturated 0.1 M KOH solution at a scan rate of 10 mV s^{-1} with different rotation speeds from 400 to 2500 rpm. (c) The Koutecky-Levich (K-L) plots of current density^{-1} versus $\omega^{-1/2}$ at various potentials obtained from LSV curves in an O_2-saturated 0.1 M KOH solution at a scan rate of 10 mV s^{-1}. (d) The number of transferred electrons calculated from the slopes of the K-L plots in (c).

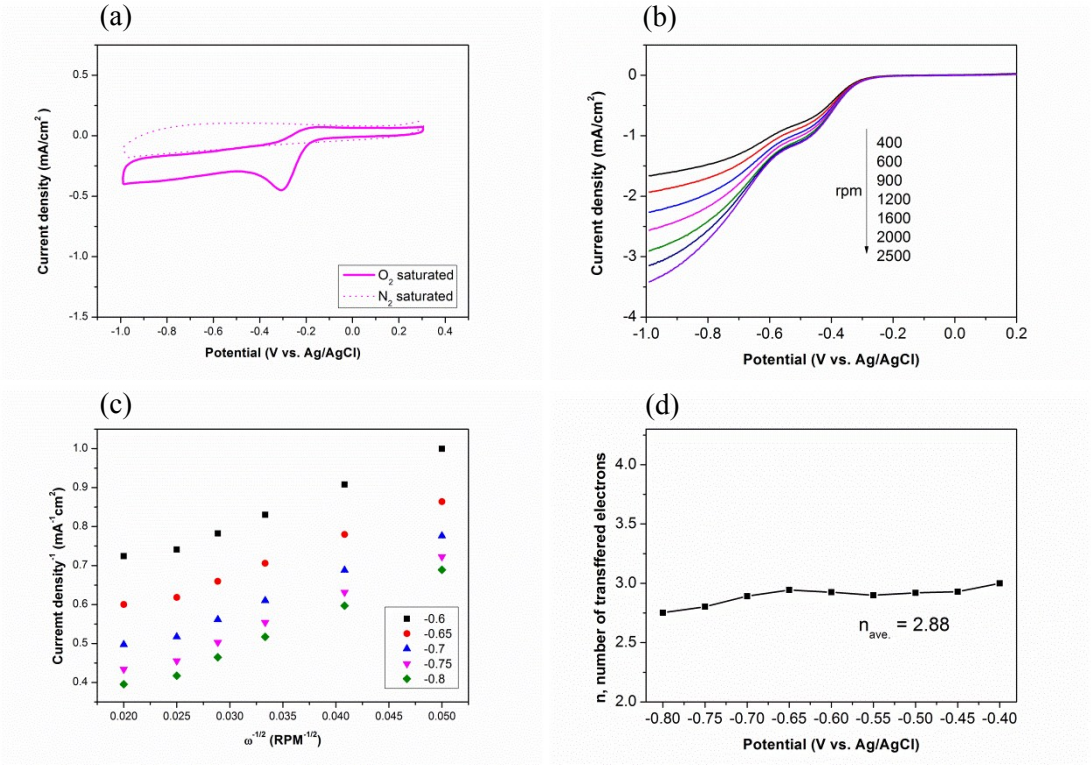

Fig. S2 Electrochemical measurements of B/N coupling: (a) CV curves of the ORR in O_2 and N_2-saturated 0.1M KOH solutions at a scan rate of 10 mV s^{-1}. (b) LSV curves of the ORR in O_2-saturated 0.1 M KOH solution at a scan rate of 10 mV s^{-1} with different rotation speeds from 400 to 2500 rpm. (c) The Koutecky-Levich (K-L) plots of current density^{-1} versus $\omega^{-1/2}$ at a various potentials obtained from LSV curves in an O_2-saturated 0.1 M KOH solution at a scan rate of 10 mV s^{-1}. (d) The number of transferred electrons calculated from the slopes of the K-L plots in (c).

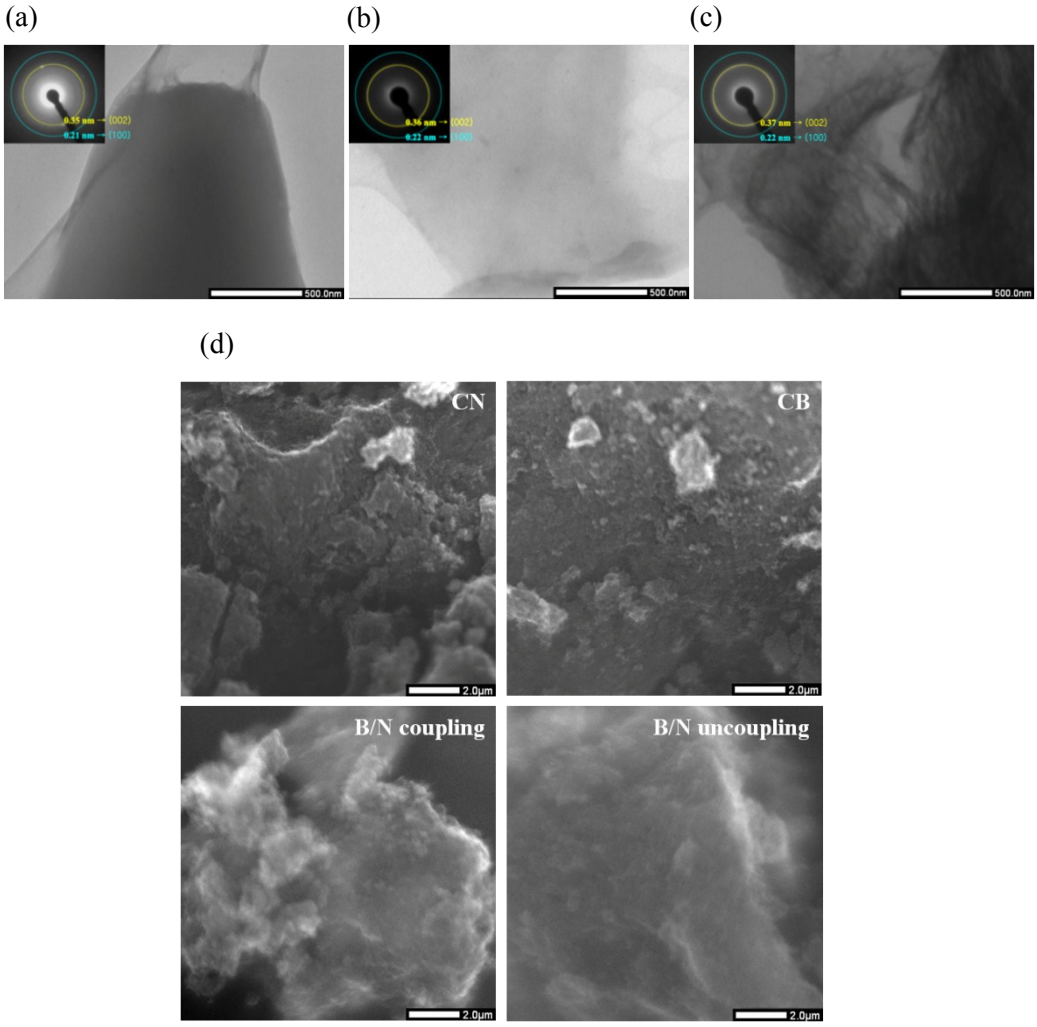

Fig. S3 Wide-field TEM images with selected-area electron diffraction (SAED) of (a) CB, (b) CN, and (c) B/N coupling. (d) SEM images of all nanocarbons.

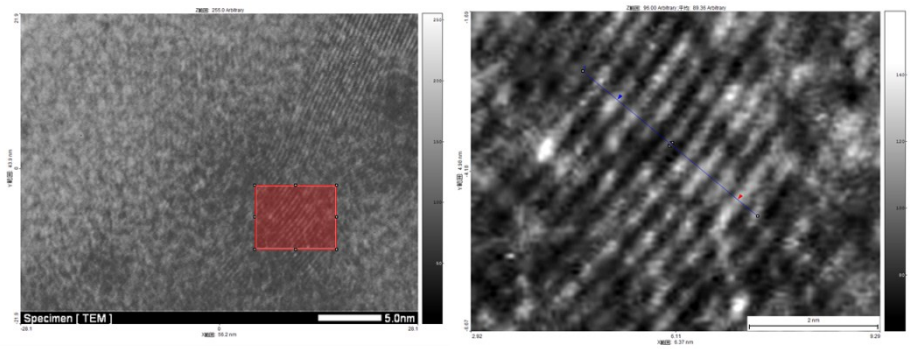

Fig. S4 Contrast line profiles of B/N uncoupling.

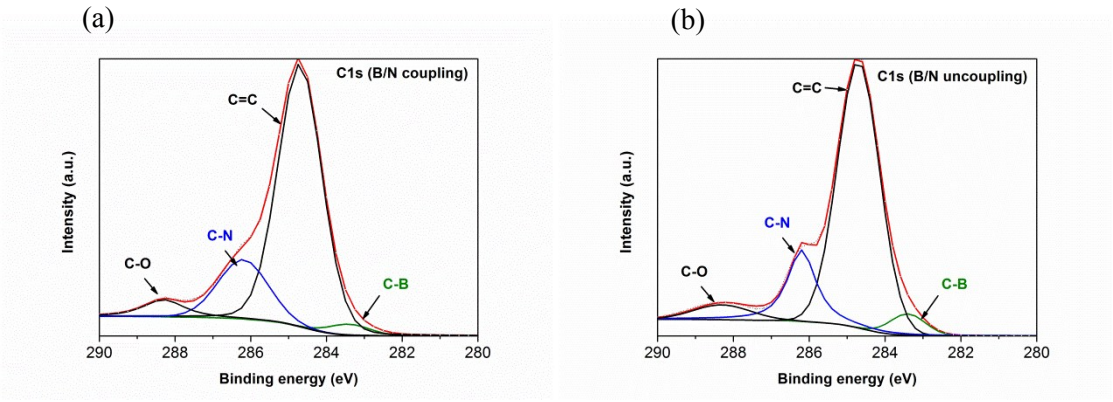

Fig. S5 Narrow scan XPS of (a) B/N uncoupling and (b) B/N coupling for C1s. The four deconvoluted peaks in the high resolution C1s spectrum at 283.4, 284.7, 286.2 and 288.3 eV can be attributed to C-B, C=C, C-N and C-O bonds, respectively. [13]

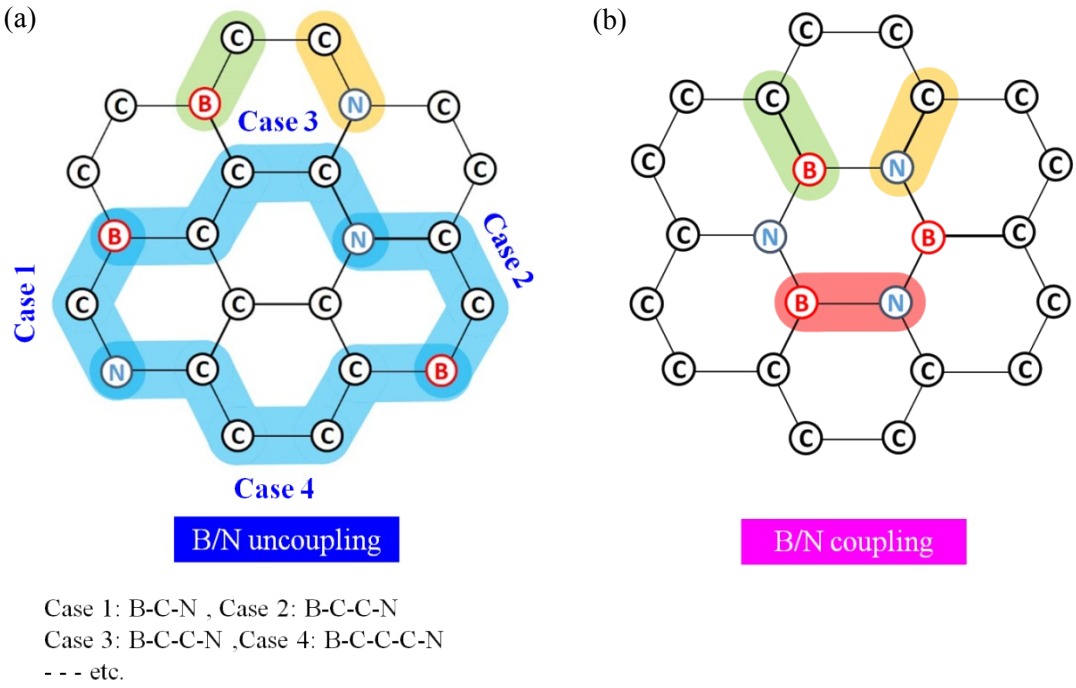

Fig. S6 Possible schematic structure of BCN nanocarbon: (a) B/N uncoupling and (b) B/N coupling.

Table S1 Relative content of (a) B atom (b) N atom and (c) Pt atom before and after chronoamperometry test.

(a) Chemical state containing B atom (%)

	B cluster	B_4C	BC_3	BC_2O	BCO_2	B_2O_3	B-N
Before	23.2	8.9	8.9	25	14.3	16.1	3.6
After	5.5	12.7	12.7	18.2	25.5	21.8	3.6

(b) Chemical state containing N atom (%)

	B-N	Pyridinic N	Pyrrolic N	Graphitic N	Oxidic N
Before	0	28.6	31.4	39.4	0.6
After	0	31.3	31.6	32.6	4.5

(c) Chemical state containing Pt atom (%)

	Pt^{4+}(4f5/2)	Pt^{4+}(4f7/2)	Pt^{2+}(4f5/2)	Pt^{2+}(4f7/2)	Pt^{0}(4f5/2)	Pt^{0}(4f7/2)
Before	2.8	3.1	7.5	11	40.8	34.8
After	4.6	5.6	15.8	20.1	26	27.9

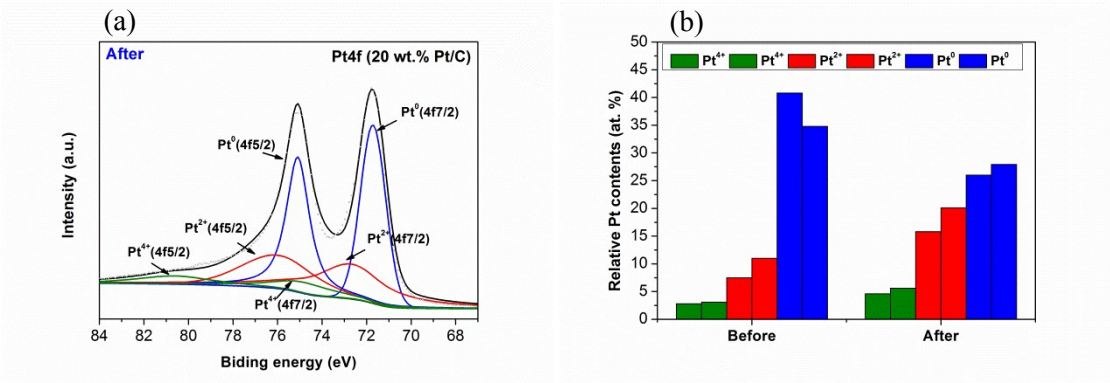

Fig. S7 XPS narrow scan after durability experiment of (a) Pt4f of 20 wt. % Pt/C and the relative element contents before and after the chronoamperometry for (b) Pt.

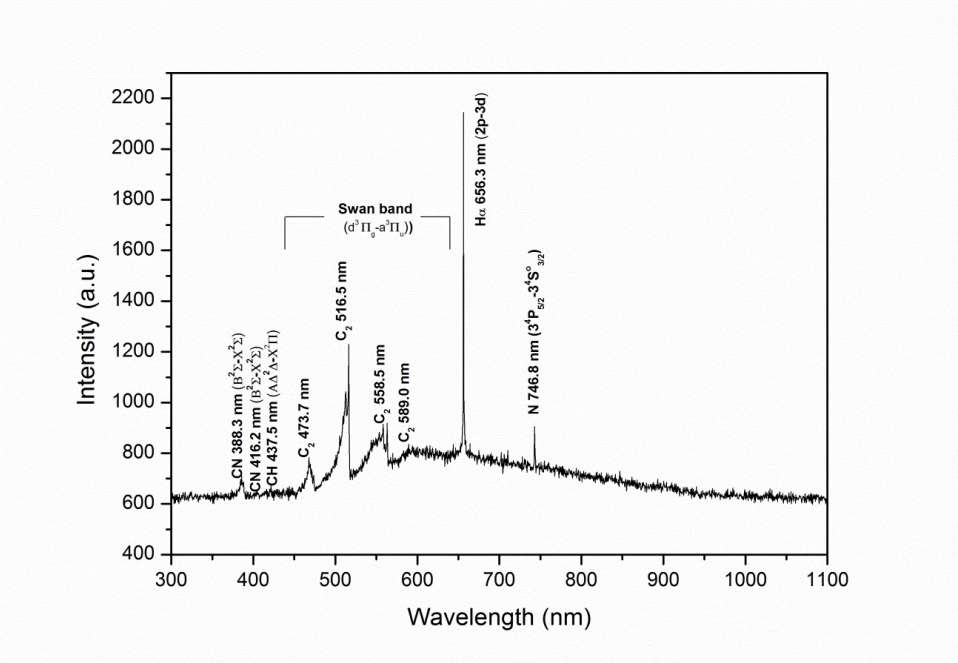

Fig. S8 OES spectra of the SPP in pure pyridine for synthesis CN (nitrogen doped carbon).