Supporting Information

Experimental

Synthesis of B-NC-x catalysts. 1.1g glucose, 1.1g basic zinc carbonate, 0.6g urea and certain amount of boric acid were mixed in a mortar. The mixture was then calcinated at 900 °C (3 °C/min) for 2 h. After cooling to the room temperature, the pyrolysis product was treated in a 1 M H_2SO_4 solution at 80 °C for 4 h. The final products were obtained after repeatedly washing by deionized water and ethanol.

Characterizations. The crystal phase of both freshly synthesized powders were detected by X-ray diffraction (XRD, Bruker AXS D8-Focus, Germany) with Cu Kα radiation in the range of 2θ from 10^o to 80^o. The micromorphology of B-NC-x and NC powders were observed by means of a field emission scanning electron microscopy (FESEM, Hitch SU8010, Japan). The X-ray photoelectron spectroscopy (XPS, Escalab 250XI, ThermoFisher, USA) was employed to further explore the composition, chemical environment and surface electronic state of the samples. All XPS profiles are aligned by C 1s (284.60 eV). The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method on the basis of the N_2 adsorption isotherm, and the mesopore distribution was analyzed by Barrett-Joyner-Halenda (BJH) method based on the data of the desorption branch using a TriStar II 3020 (Micromeritics Instrument Corporation, USA). The Raman spectra of as-obtained B-NC-x and NC catalysts were acquired using a Renishaw System RM-1000 spectrometer. The B content of all samples were measured by Inductively coupled

plasma mass spectrometry (ICP-MS), the C and N content of all samples were provided by Elemental analysis.

Electrochemical measurements. All the electrochemical measurements were performed on a CHI 760E electrochemical workstation with a typical three-electrode system configuration in 1 M KOH electrolyte saturated with N_2 or O_2. Typically, 2 mg Vulcan XC-72R carbon black and 2 mg respectively of commercial 20 wt% Pt/C (Johnson Matthey HiSPEC 3000 purchased at Alfa Aesar) powder or as-prepared B-NC-x catalyst were dispersed in 650 μL deionized water, 300 μL ethanol and 50 μL Nafion solution via ultrasonic treatment for 1h to obtain a homogeneous dispersion. Subsequently, 144 μL of the resulting ink (containing 288 μg of catalyst) was pipetted on the surface of rotating disc electrode (RDE) in a diameter of 4 mm and then air-dried, i.e. catalyst mass loading was 2.29 mg cm^{-2}. LSV at a scan rate of 5 mV s^{-1} was performed under O_2 -saturated 1 M KOH electrolyte using RDE coated with various catalysts as the working electrode at a rotating speed of 1600 rpm, graphite rod as the counter electrode and Hg/HgO electrode as the reference electrode. Cyclic Voltammetry (CV) was conducted at a scan rate of 50 mV s^{-1} ranging from 0.2 to 1.1 V. vs. RHE. The reference electrode, Hg/HgO, was calibrated with respect to the reversible hydrogen electrode (RHE), ERHE =EHg/HgO+0.059×pH+0.099. For the chronoamperometric (I-t) response investigation, the working electrode was biased at ERHE=0.6V in alkaline media for 35000s. The ORR stability was also evaluated by comparing the LSV curves before and after 10000 CV cycles (across the potential window of 0.1–0.4 V vs. RHE) at a

sweep rate of 50 mV s^{-1}. The peroxide yields (HO_2^-%) and the electron transfer number (n) are calculated with the following equation.

$$HO_2^-\% = \frac{200 i_r}{N(i_d + \frac{i_r}{N})} \qquad n = \frac{4 i_d}{i_d + \frac{i_r}{N}}$$

Where Id is the disk current, Ir is the ring current, and N is the current collection efficiency of the Pt ring. (Measured value N=0.26)

The RDE tests were measured at various rotating speeds ranging from 400 to 2025 rpm with a sweep rate of 5 mV s−1. The electron transfer number (n) can be calculated using Koutecky-Levich equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{J_K} \qquad B = 0.62nFC_0D_0^{\frac{2}{3}}V^{-\frac{1}{6}}$$

where J is the measured current density, J_K and J_L are the kinetic and limiting current densities, ω is the angular velocity of the disk, n is the electron transfer number, F is the Faraday constant (96485 C mol^{-1}), C_0 is the bulk concentration of O_2 (1.2 × 10-6 mol cm^{-3}), D_0 is the diffusion coefficient of O_2 in 1 M KOH (1.93 × 10^{-5} cm^2 s^{-1}), and V is the kinematic viscosity of the electrolyte (0.01 cm^2 s^{-1}).

All of the potentials reported in this study were referenced to a reversible hydrogen electrode (RHE) and all of the current densities reported in in this study were normalized by geometric area of electrode.

Supplementary Results

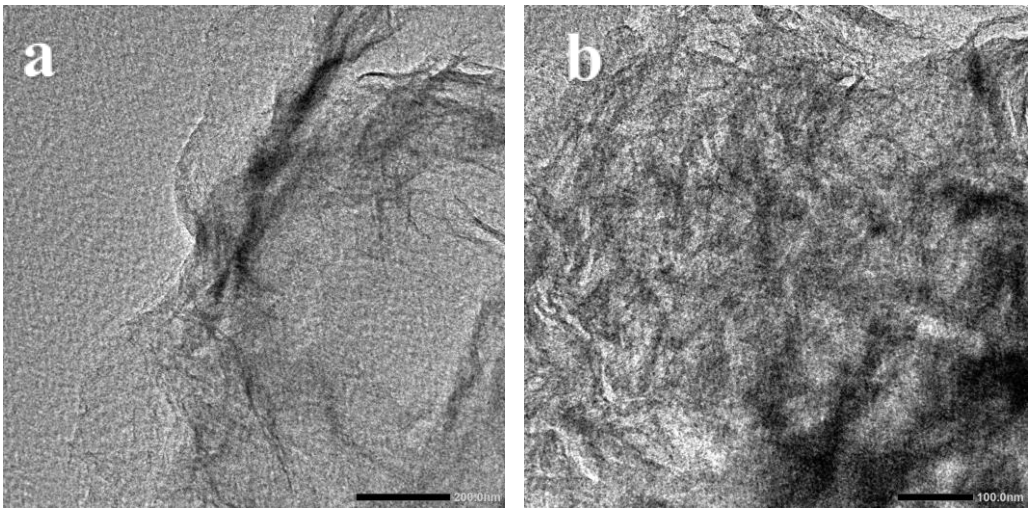

Figure S1. TEM images of B-NC-2.

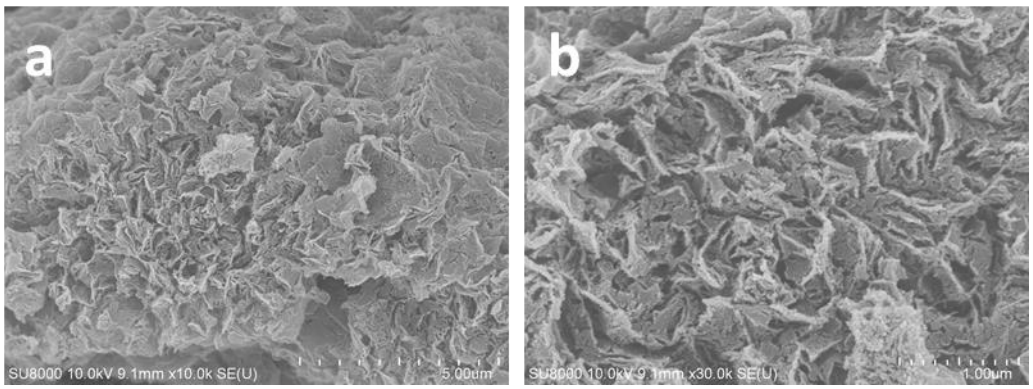

Figure S2. SEM images of the B-NC-0 catalyst.

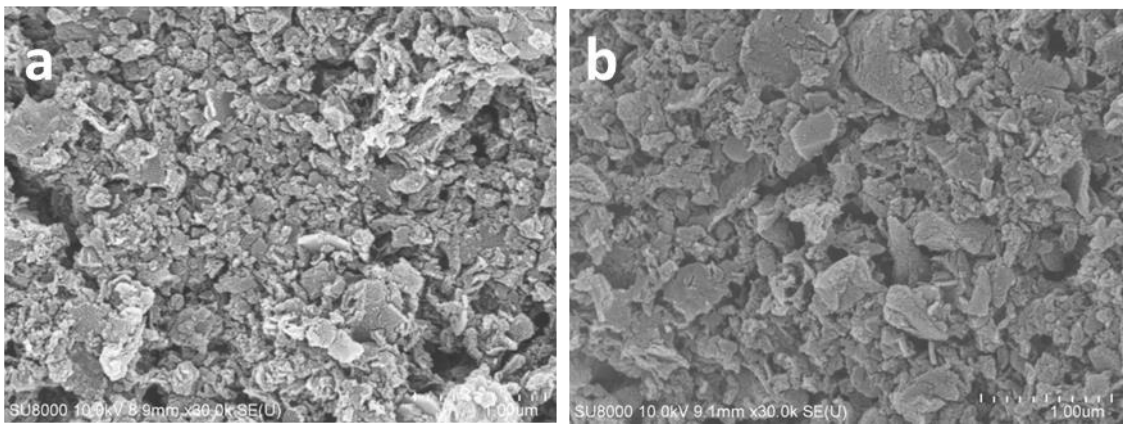

Figure S3. SEM images of (a) B-NC-1 and (b) B-NC-3.

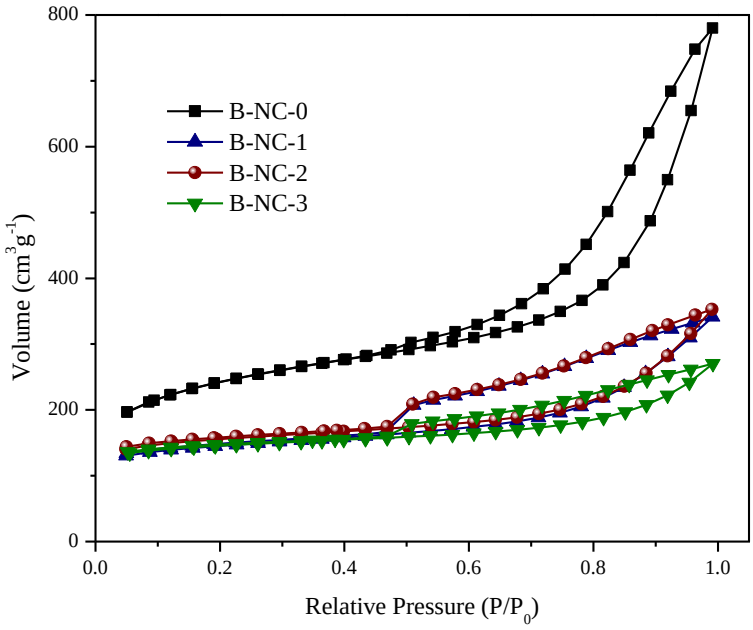

Figure S4. Nitrogen sorption isotherms of the B-NC-x catalysts.

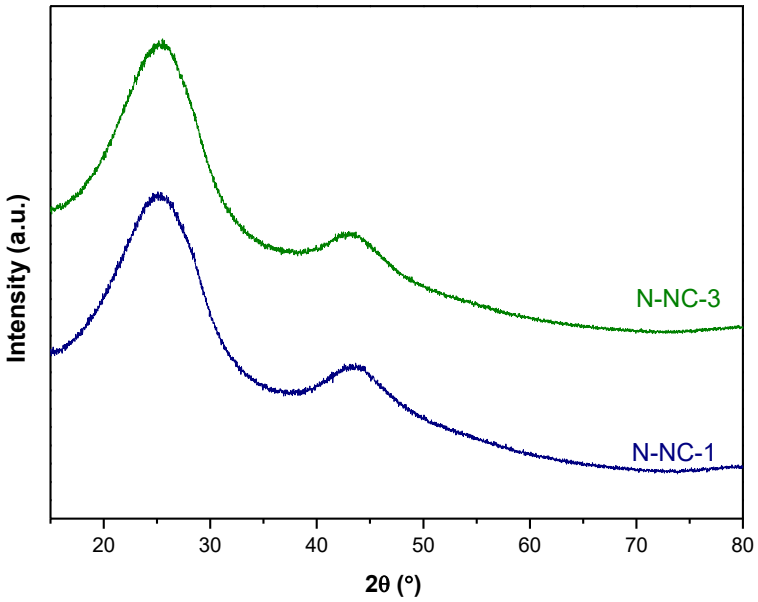

Figure S5. XRD patterns of the B-NC-1 and B-NC-3 catalysts.

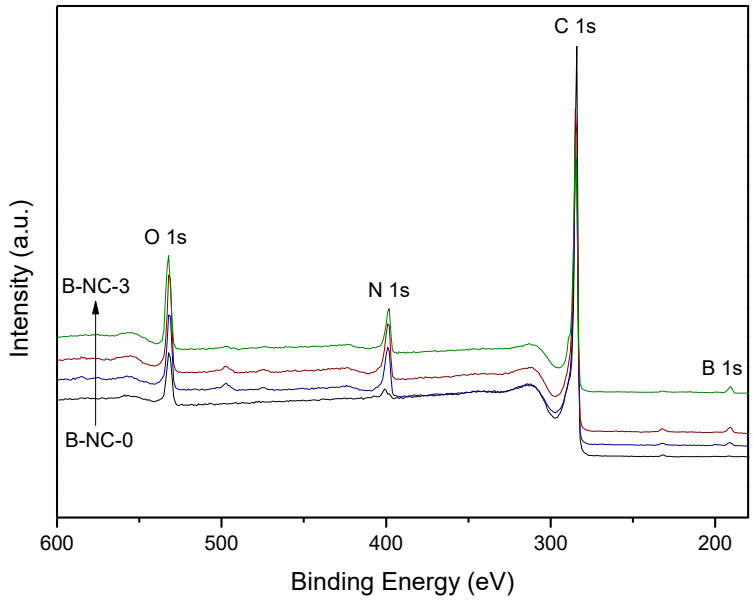

Figure S6. XPS survey spectra of the B-NC-x catalysts.

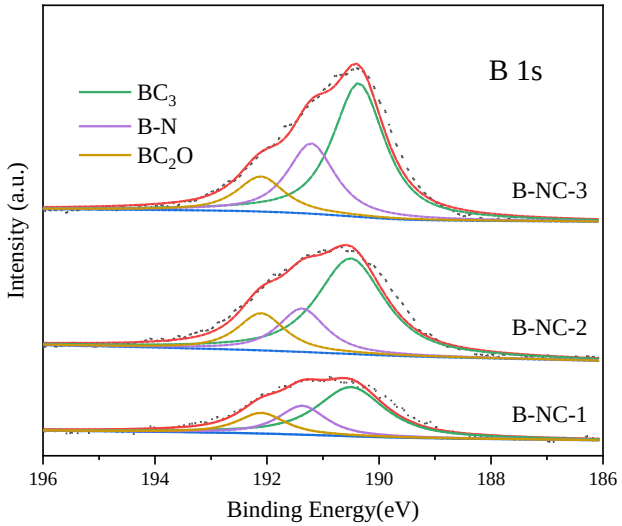

Figure S7. Deconvoluted B 1s XPS spectra of the B-NC-1, B-NC-2 and B-NC-3 catalysts.

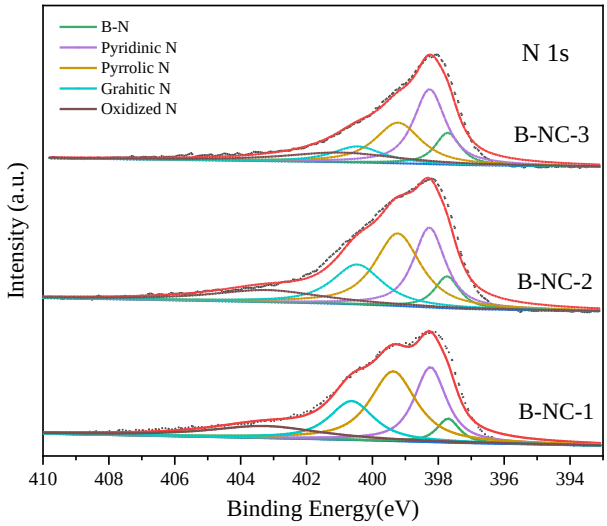

Figure S8. Deconvoluted N 1s XPS spectra of the B-NC-1, B-NC-2 and B-NC-3 catalysts.

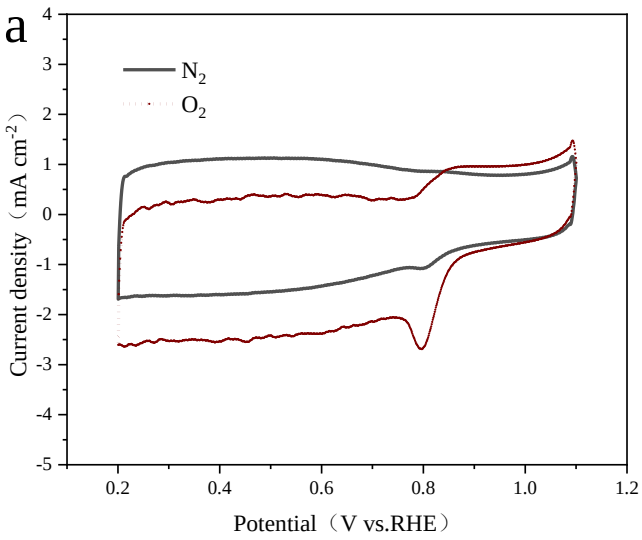

Figure S9. CVs of B-NC-2 in N_2/O_2-saturated 1 M KOH at a scan rate of 50 mV s^{-1}.

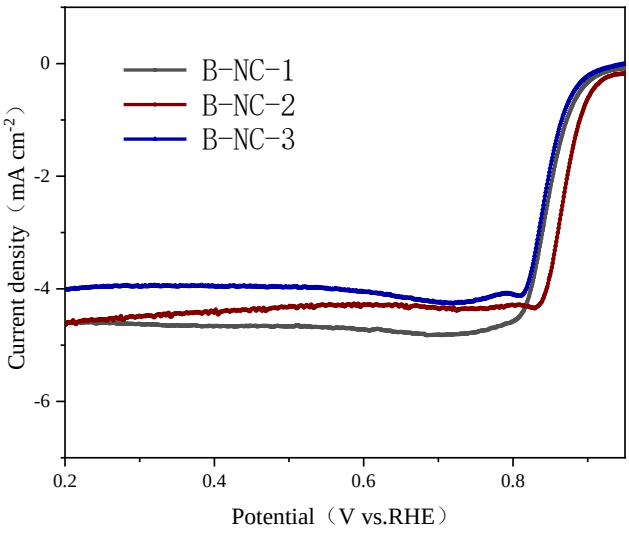

Figure S10. LSV curves of B-NC-1, B-NC-2 and B-NC-3 at a scan rate of 5 mV s^{-1}.

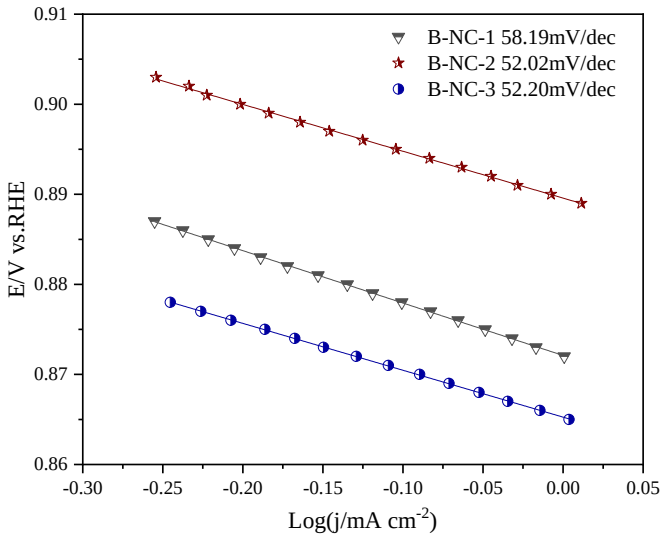

Figure S11. Tafel plots of B-NC-1, B-NC-2 and B-NC-3.

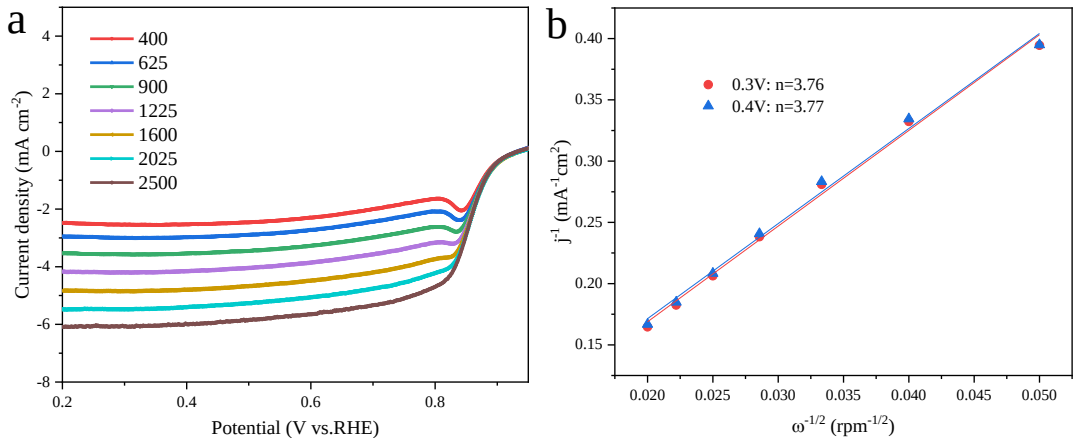

Figure S12. LSV curves of B-NC-2 at different rotating speeds and (b) electron transfer number of B-NC-2.

Table S1. Bulk elemental composition of the B-NC-x catalysts provided by Elemental analysis (N and C) and inductively coupled plasma – mass spectrometry analysis (B).

	B (wt.%)	N (wt.%)	C (wt.%)
B-NC-0	0	1.04	78.39
B-NC-1	0.95	9.73	62.67
B-NC-2	1.83	10.13	59.91
B-NC-3	1.97	10.96	58.95

Table S2. The content of pyrrolic N and pyridinic N in the catalysts.

	pyridinic N (Atomic %)	pyrrolic N (Atomic %)
B-NC-0	0.33	0.14
B-NC-1	2.89	3.85
B-NC-2	2.96	3.83
B-NC-3	2.94	3.67