Supporting information

for

Boron and nitrogen dual-doped carbon nanospheres for efficiently electrochemical reduction of N$_2$ to NH$_3$

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Experimental section

Materials: All chemicals (melamine, boric acid, glucose and ethanol) were analytical grade and used as received without further purification obtained from Sino pharm Chemical Reagent Co , Ltd.

Synthesis of electrocatalyst: Primarily, the C_3N_4 were prepared from melamine via thermal method. In a typical procedure, 5 g of melamine was stuffed into a porcelain boat with a cap and annealed in a tube furnace at 550 °C in argon atmosphere for 4 h with a heating rate of 5 °C min^{-1}. C_3N_4 was obtained after cooling. Secondly, to synthesize the C_3N_4 with glucose coating (C_3N_4-Glu), 0.4 g of C_3N_4 and 3.26 g of glucose were dispersed in 50 mL of ultrapure water for 4 h by sonication. The resulting brownish yellow solution was sealed in a 100 mL Teflon-lined stainless steel autoclave and held at 180 °C for 10 h. The product (C_3N_4-Glu) was collected and washed three times with a filter paper (220 μm) through a vacuum filtration apparatus using ultrapure water and absolute ethanol, and then dried overnight in an oven at 70 °C. The C_3N_4-Glu was mixed with boric acid in a weight ratio of 3:1, and the mixture was dispersed in 50 mL of ultrapure water with continuous stirring and kept at 80 °C until the water evaporated. The resulting composite was annealed at 900 °C for 3 h in an argon atmosphere at a heating rate of 5 °C min^{-1} to form BCN-NS. As comparison, C_3N_4-Glu products were independently calcined at 900 °C for in an Argon atmosphere 1 h to form NC-NS.

Material characterization: The morphologies and microstructures of the samples were observed by a scanning electron microscope (SEM) at an accelerating voltage of 5 kV (SU8010, HITACHI, Japan). Energy dispersive spectroscopy (EDS) analysis was performed at the acceleration voltage of 200 kV using a TECNAI G2 F20 (FEI Ltd., USA) TEM equipped with a Bruker X Flash 5030 detector (Bruker Nano GmbH, Berlin, Germany). The specific surface are (BET) and pore volume were collected at a Micromeritics ASAP 2460 apparatus and porosity analyzer. N_2 adsorption property measurements were conducted on a temperature-programmed desorption (TPD) apparatus Micromeritics ASAP 2020 using helium as carrier gas, and the adsorbed amount was calculated from thermal conductivity signals. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) were used to investigate the surface composition of samples. The electro-catalyst powder was placed on indium substrate and measured under high vacuum atmosphere. During the calibration process set C1s peak was fixed at 284.5 eV as standard. The absorbance data of spectrophotometer were recorded on SPECORD PIUS200 UV-Vis spectrophotometer.

Electrochemical measurement: All electrochemical testing were recorded at room temperature using the Reference 1000 Gamry. The electrochemical testing was accomplished in a three electrode system. Glassy carbon electrode with a diameter of 3 mm (GCE) and a saturated calomel electrode (SCE) and a carbon rod were used as working, reference and counter

electrodes. NRR electrocatalytic activity was carried out in a N_2 saturated 0.05 M H_2SO_4 solution in an H-type electrochemical cell, which was separated by a Nafion 211 membrane. The membrane was boiled in ultrapure water for 1 h, then heated to 80°C in H_2O_2 (5 %) for 1 h and finally boiled in sulfuric acid (0.5 M) for 2 h. All the potentials in this manuscript were converted to the RHE reference scale using E (vs. RHE) = E (vs. SCE) + 0.0591 × pH + 0.244 V.

Ammonia calculation: NRR electrolysis experiment was tested in 0.05 M H_2SO_4 and the NH_3 concentration was spectrophotometrically determined by the method of indophenol blue. 2 mL of electrolyte was obtained from the cathodic chamber and then added 1 M NaOH solution containing 5% salicylic acid and 5% sodium citrate to the electrolyte. Thereafter, 1 mL of 0.05 M NaClO and 0.2 mL of 1% sodium nitroprusside were added to the above solution. The UV-vis absorption spectrum was measured at 655 nm. The NH_3 accumulation-absorbance curves were plotted with a list of concentration of standard NH_3 solution. It showed an excellent linear relationship between the absorbance value and the $(NH_4)_2SO_4$ concentration from the fitting curve (y = 0.3938x + 0.0342, R^2 = 0.999).

FE and NH_3 yield rate: The FE of N_2 reduction was evaluated as the amount of electric charge used for synthesizing NH_3 divided the total charge passed through the electrodes during the electrolysis. The total amount of NH_3 produced during NRR electrolysis experiments was measured using

colorimetric methods. Assuming three electrons were needed to form a NH_3

molecule, the calculation method of FE is not difficult to derive as:

$FE=(3\times F\times C_{NH3}\times V)\times(17\times Q)^{-1}$

The rate of NH_3 formation (V_{NH3}) can be measured using the following

formula:

$V_{NH3}=C_{NH3}\times V\times(t\times m_{cat})^{-1}$

F represents the Faraday constant, C_{NH3} is the measured amount of NH_3

accumulation, V is cathode chamber electrolyte volume, t is the NRR testing

time and m_{cat} is the catalyst loading on the electrode.

Nuclear magnetic resonance (NMR) spectroscopy: In the electrocatalytic

N_2 reduction experiment, Argon gas was purged to the cathodic cell to remove

impurity gas and then purging for 30 min with the gas to be tested. After

electrolysis at -0.4 V vs. RHE for 2 h, 50 mL of the electrolyte was taken out

and acidized to pH 3 by adding H_2SO_4 (pH=1), and then concentrated to 5 mL

by heating via reduced pressure distillation. Afterwards, 0.55 mL of the

resulting solution was taken out and mixed with 0.05 mL D_2O for ^1H-NMR

measurement. A total of 1024 transient scans were recorded with an inter-

scan delay of 1 s. 64 K complex points was acquired for each FID with an

acquisition time of 3.4 s. The produced ammonia was quantitatively detected

by using ^1H-NMR means on a Bruker AVANCE III HD 400 instrument. A

known amount of D_2O was used as an internal standard. By analyzing the

acquired spectra, $^{15}NH_4^+$ calibration curve was obtained by integrating the

ammonia signal appeared at 7.00 ppm as a function of prepared known

$(^{15}NH_4)_2SO_4$ (from Aladdin) standard solution dissolved in 0.1 M H_2SO_4.

Table S1 Quantitative analysis of XPS spectra of BNC-NS before and after CA test.

	C1s (%)	N1s (%)	B1s (%)
Before CA test	87.7	7.9	4.4
After CA test	87.6	7.9	4.5
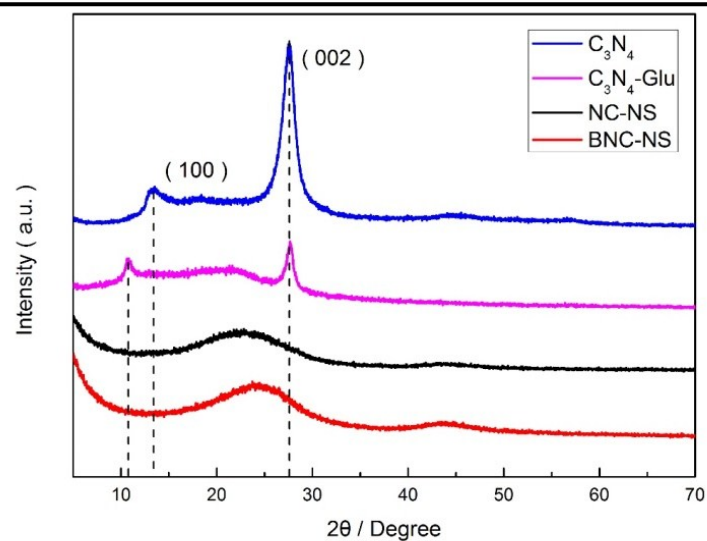
Figure S1 XRD patterns of C_3N_4, C_3N_4@Glu, NC-NS and BNC-NS electrocatalysts.
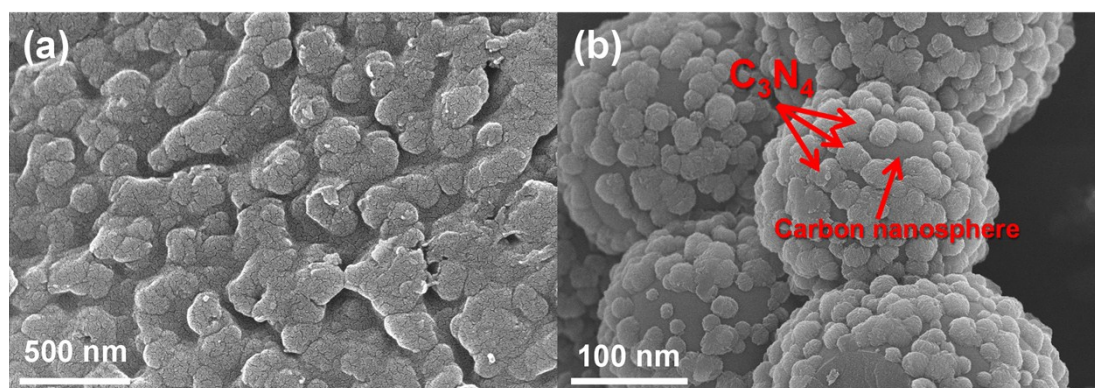
Figure S2 SEM images of C_3N_4 and C_3N_4@Glu electrocatalyst.
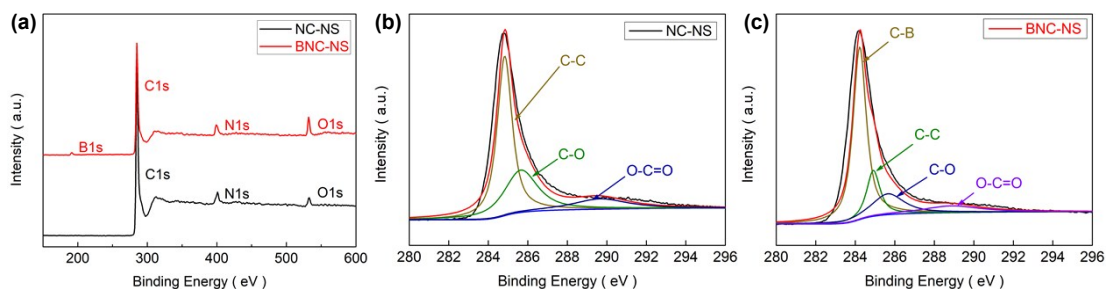
Figure S3 XPS survey scan (a) and deconvoluted C1s peaks of NC-NS (b) and BNC-NS (c) electrocatalysts.
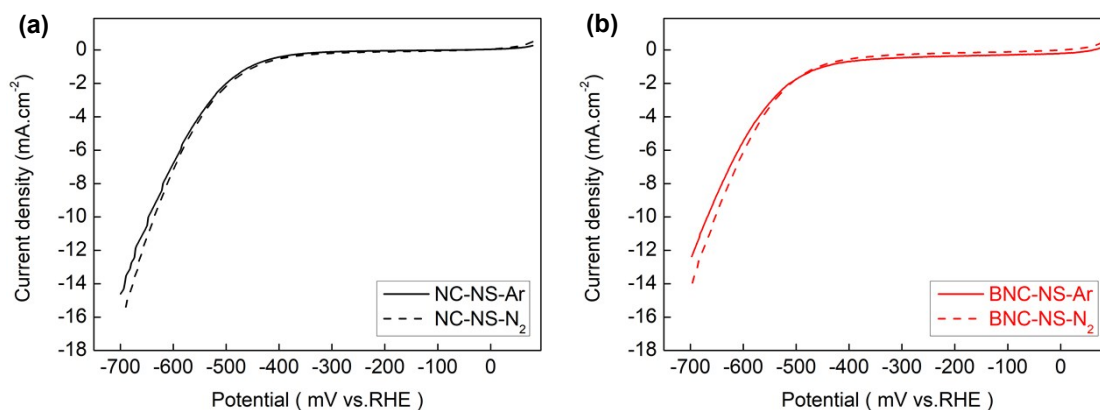
Figure S4 LSV curves of NC-NS (a) and BNC-NS (b) electrocatalysts recorded in Ar- (solid line) and N_2-saturated (dotted line) 0.05 M H_2SO_4 electrolyte.
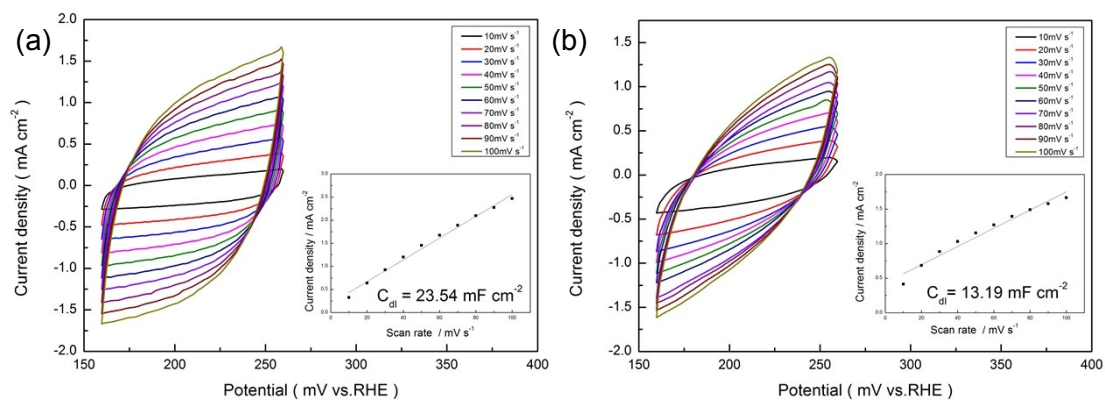
Figure S5 CV curves of NC-NS and BNC-NS electrocatalysts measured from 0.16 to 0.26 V vs. RHE.
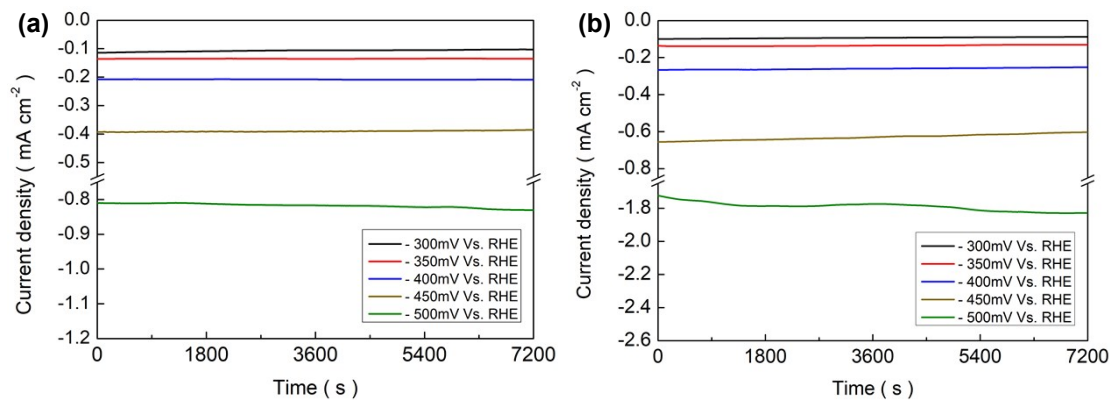
Figure S6 Chronoamperometric curves of BNC-NS (a) and NC-NS (b) electrocatalyst with different applied potentials.
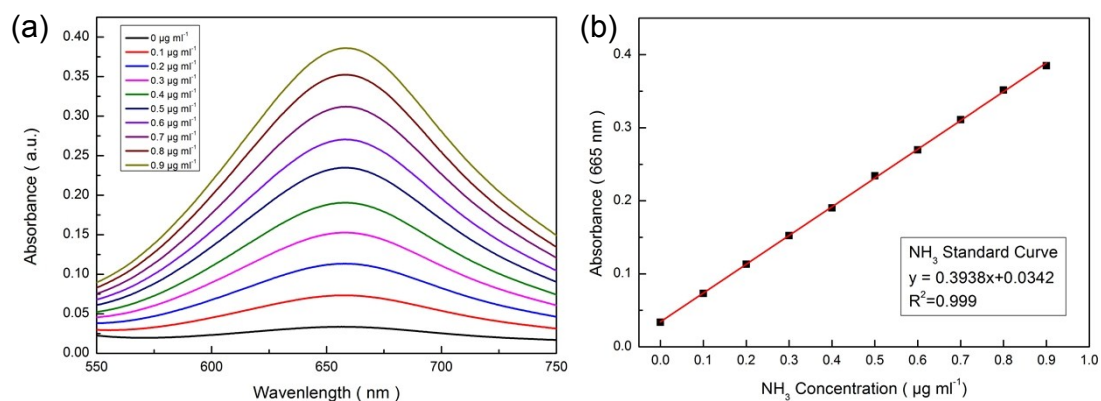
Figure S7 UV-vis spectroscopies of colorimetry and calibration of colorimetric NH$_3$ assay by salicylic acid spectrophotometry.
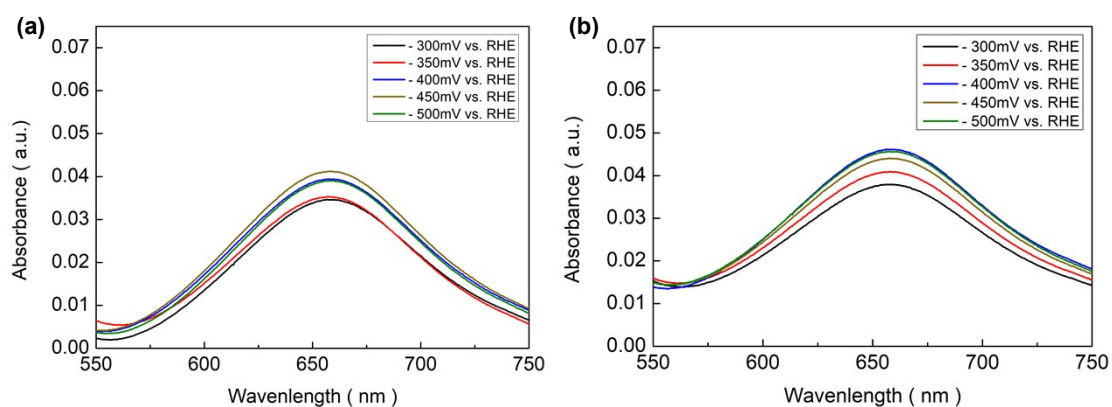
Figure S8 UV-vis spectroscopies of the electrolyte after testing with NC-NS (a) and BNC-NS (b) electrocatalyst in 0.05 M H$_2$SO$_4$ electrolyte.
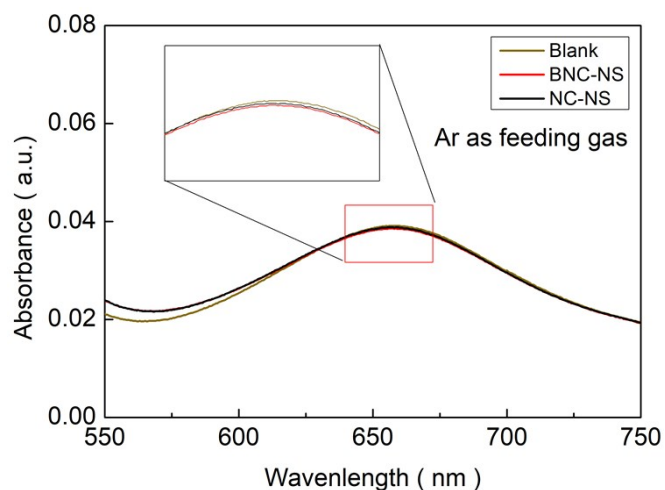
Figure S9 UV-vis spectroscopies of the electrolyte after testing with NC-NS and BNC-NS electrocatalyst in Ar-saturated 0.05 M H_2SO_4.
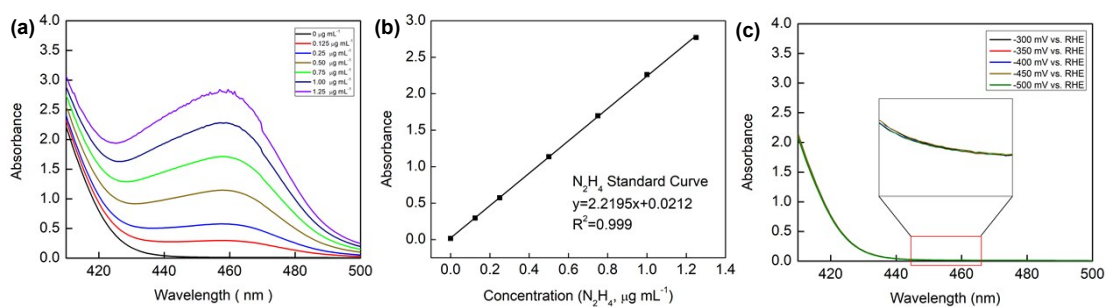
Figure S10 UV-vis spectroscopies of N_2H_4 (a, b) assay by salicylic acid spectrophotometry. (c) UV-vis spectroscopies of electrolytes after NRR catalysis with various applied potentials.
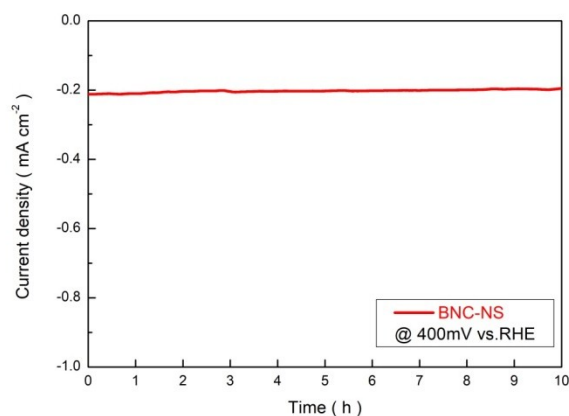
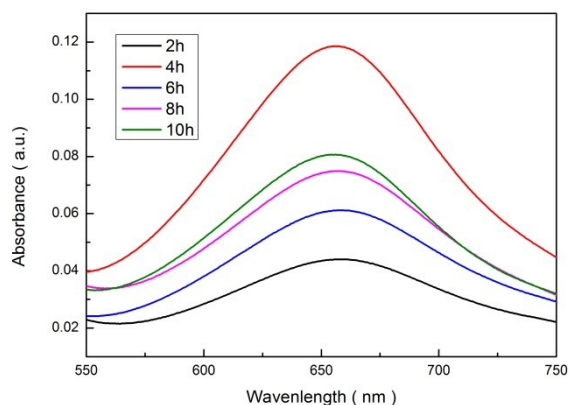**Figure S11** Chronoamperometric test of BNC-NS at -400 mV vs. RHE for 10 h.

Figure S12 UV-vis spectroscopies of the electrolyte after testing with BNC-NS electrocatalyst for different times at -400 mV vs. RHE in 0.05 M H_2SO_4 electrolyte.
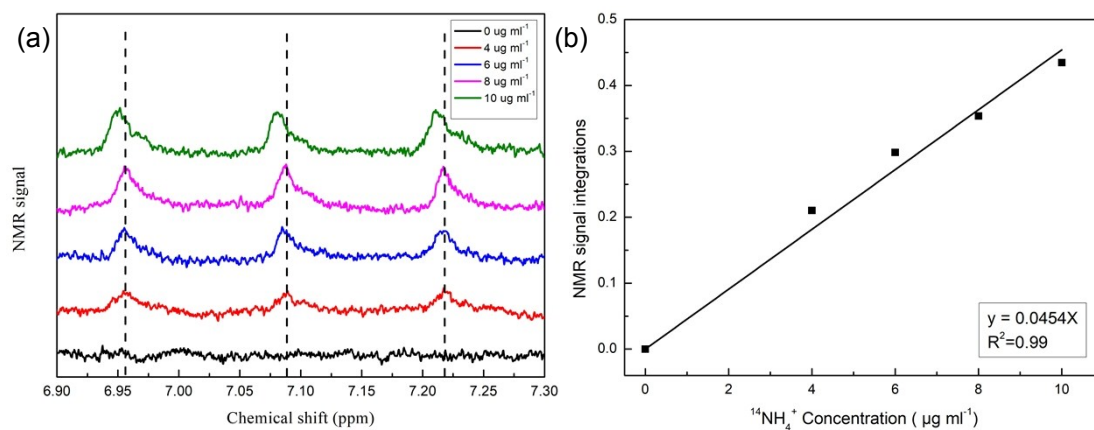
Figure S13 (a) NMR spectra of $(^{14}NH_4)_2SO_4$ with different concentration. (b) Standard curve of NMR intensity as a function of $(^{14}NH_4)_2SO_4$ concentration.
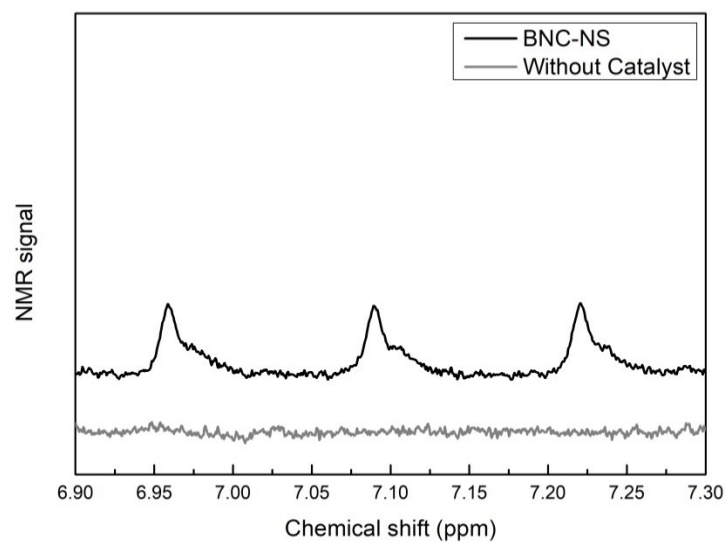
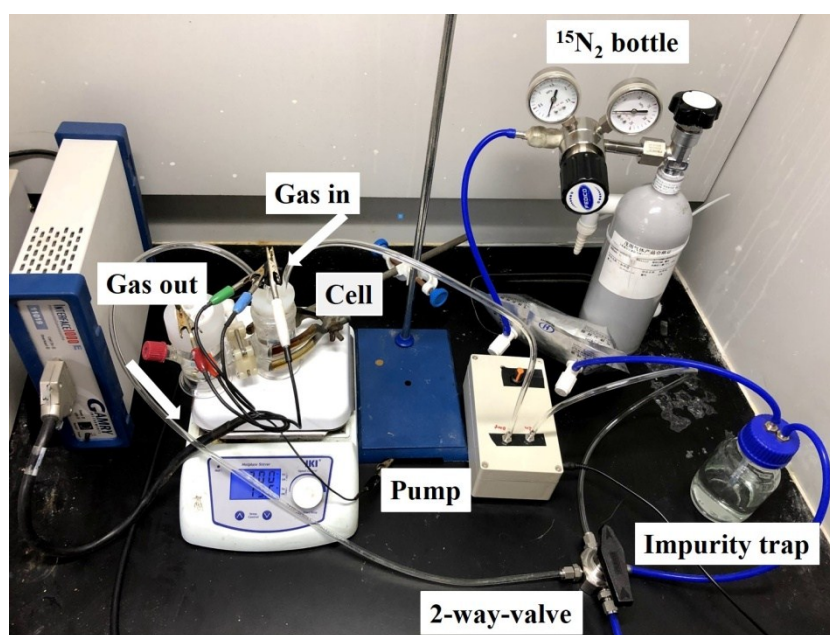**Figure S14** NMR spectra of the production after NRR at -400 mV vs. RHE with (black line) and without (grey line) BNC-NS electrocatalyst.

Figure S15 Setup for NRR catalysis using $^{15}N_2$ as feeding gas.
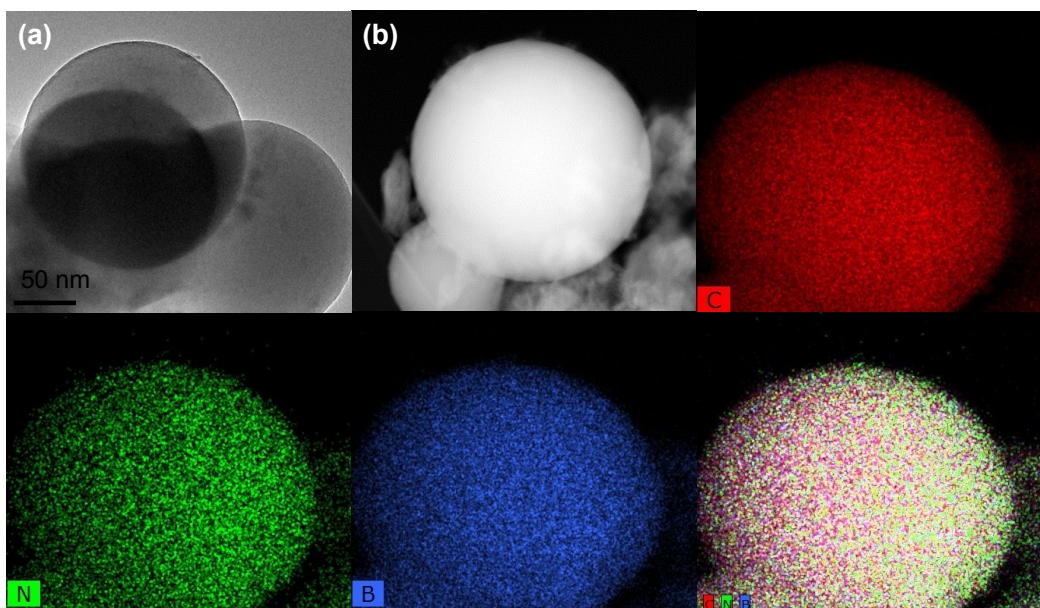
Figure S16 SEM (a), TEM (b), HAADF-STEM (c) images and relative EDS mappings of C, N and B elements of BNC-NS electrocatalyst after stability test.
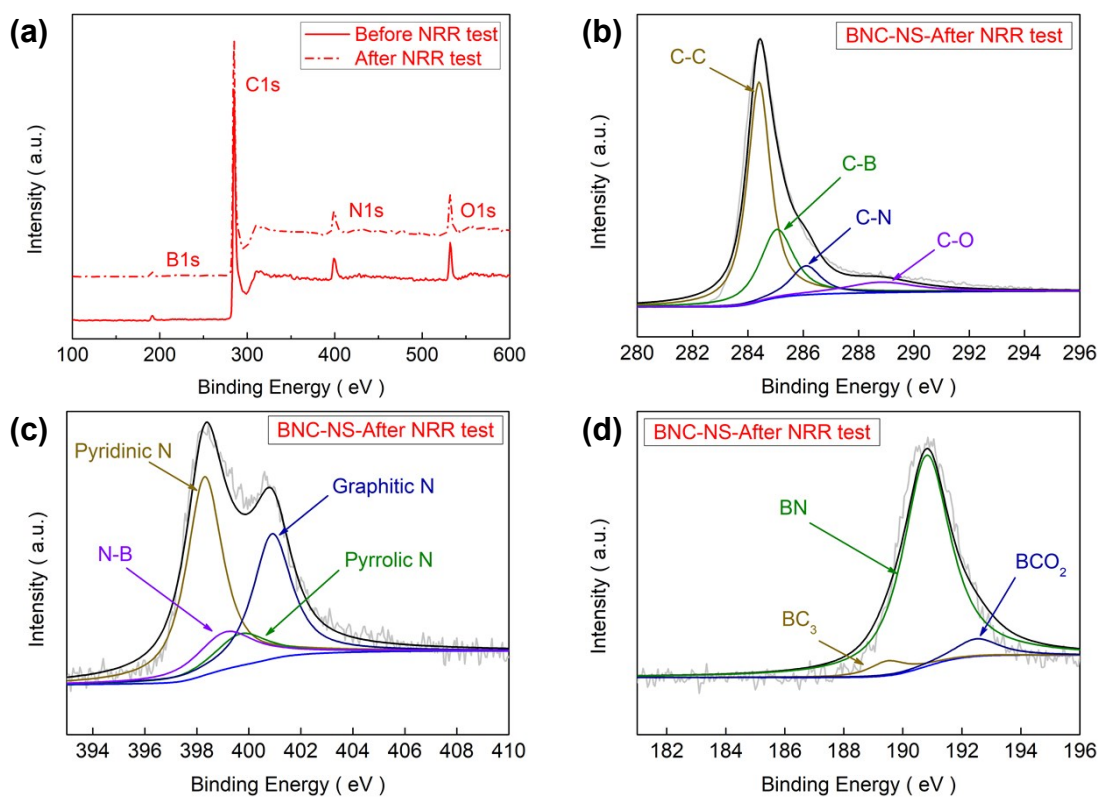

Figure S17 XPS survey scan (a), deconvoluted C1s (b), N1s (c) and B1s (d) peaks of BNC-NS electrocatalyst after CA test.
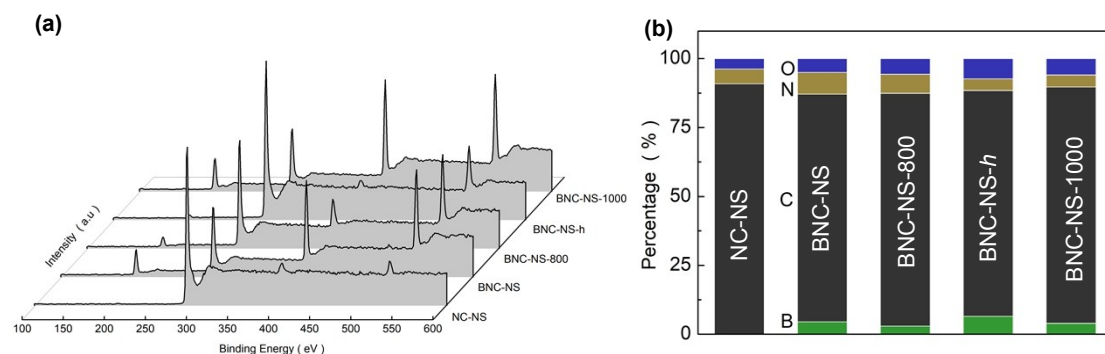
Figure S18 (a) XPS survey scan of different electrocatalysts. (b) Calculated element contents of various electrocatalysts.
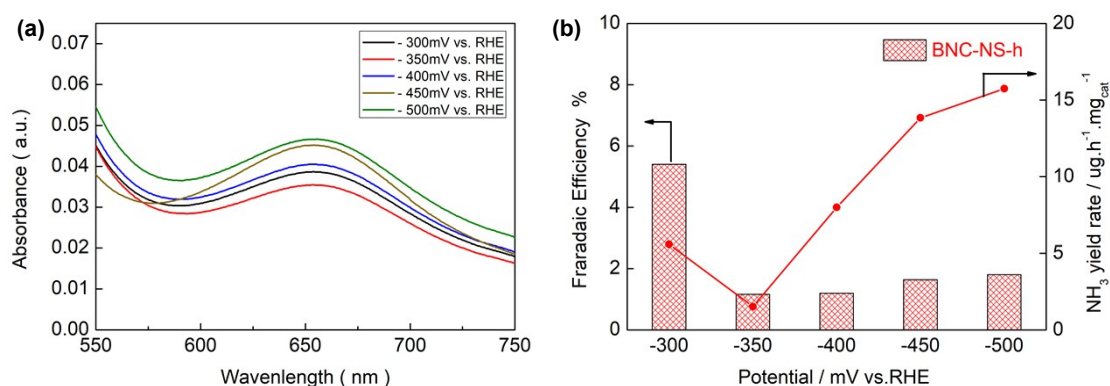

Figure S19 (a) UV-vis spectroscopies of the electrolyte after testing with BNC-NS-*h* electrocatalyst for different times at -400 mV vs. RHE in 0.05 M H$_2$SO$_4$ electrolyte. (b) Calculated Faradaic Efficiency and NH$_3$ yield rate.
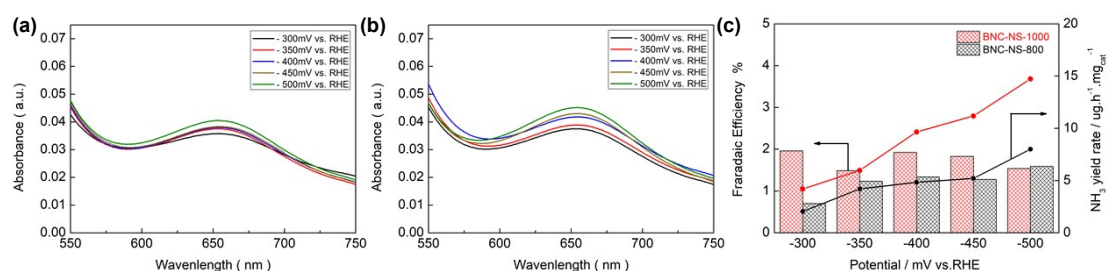

Figure S20 UV-vis spectroscopies of the electrolyte after testing with BNC-NS-800 (a) and BNC-NS-1000 (b) electrocatalyst for different times at -400 mV vs. RHE in 0.05 M H$_2$SO$_4$ electrolyte. (c) Calculated Faradaic Efficiency and NH$_3$ yield rate.