## Supporting Information

# Biomass-Derived Nitrogen-Doped Porous Carbon for Highly Efficient Ambient Electro-Synthesis of NH<sub>3</sub>

Qinglin Li <sup>1, 2</sup>, Xiufang Chen <sup>1, 3</sup>, and Yong Yang <sup>1,\*</sup>

- Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao
   266101, P R China
- <sup>2</sup> University of Chinese Academy of Sciences, Beijing 100049, P R China
- <sup>3</sup> National Engineering Lab for Textile Fiber Materials & Processing Technology (Zhejiang) Zhejiang Sci-Tech University Hangzhou 310018, P R China
- \* Correspondence: yangyong@qibebt.ac.cn (Y.Y.)

#### 1. Characterization

The X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance diffractometer equipped with Cu<sub>Ka</sub> radiation ( $\lambda$  = 1.5147 Å). Transmission electron microscope (TEM) images were recorded using a H-7600, high-resolution TEM (HRTEM) and scanning transmission electron microscope (STEM)and images were recorded using Tecnai G2 F30. Nitrogen adsorption-desorption isotherms were performed on a Micromeritics ASAP 2020 static volumetric sorption analyzer. The Brunauer-Emmet-Teller (BET) method was conducted to calculate the specific surface area of the sample. The micropore volume was calculated through the t-plot method. The pore size distributions were determined by non-local density functional theory (NLDFT). The X-ray photoelectron spectroscopy (XPS) analyses were conducted on an ESCALAB 250Xi (Thermo Scientific, UK) instrument using an AlK $\alpha$  line source. The elemental composition analysis were recorded using a Vario El elemental analyzer. The Raman spectra were measured on a Horiba Jobin Yvon LabRAM HR800. The absorbance data of electrolyte were abtained by a UV-Vis spectrophotometer (Lambda 25, PerkinElmer). N<sub>2</sub> temperatureprogrammed desorption (N2-TPD) measurements were conducted on AutoChemII 2920 (Micromeritics, America). The samples were first pretreated at 300 °C for 1 hour in a 50 mL/min He stream and then cooled to 50 °C under a He atmosphere. These samples were adsorbed to N<sub>2</sub> for 3 hours, and the remaining N<sub>2</sub> was purged by He for half an hour. Finally, the desorption of N<sub>2</sub> was carried out by heating from 50 °C to 600 °C at a rate of 5 °C min<sup>-1</sup>. 1H NMR spectra were collected on a superconducting-magnet NMR spectrometer (Bruker Avance III HD 600 MHz) and dimethyl sulphoxide was used as an internal to calibrate the chemical shifts in the spectra. The NH<sub>4</sub><sup>+</sup> ion concentration was detected on a ion chromatography (ICS-3000, DIONEX).

#### 2. Preparation of NC

Typically, the powder of bamboo shoots was prepared through dried and grounded of fresh bamboo shoots. Then, the powder was processed via hydrothermal method using deionized water at 180°C to obtain the biochar, which was then filtered, washed thoroughly with deionized water and dried under vacuum at 60°C. Finally, the acquired brown biochar was pyrolyzed at 600, 800, and 1000°C, respectively, under a N<sub>2</sub> atmosphere for 4 h at the heating rate of 5°C min<sup>-1</sup>.

#### 3. NRR measurements

Electrochemical NRR experiments were carried out in a gas-tight H-cell, which cathode and anode chambers isolated by a Nafion N115 membrane by using a CHI 660 electrochemical analyzer. The electrochemical NRR activity of NC were performed in a three-electrode system in 0.1 M HCl by using the working electrode, platinum foil counter electrode, and Ag/AgCl (saturated KCl electrolyte) reference electrode. All potentials were calculated to the reversible hydrogen electrode (RHE) by Eq.(1)

$$E$$
 (vs. RHE)=E (vs. Ag/AgCl)+0.059×pH+0.197 V (1)

All electrolysis tests were conducted at room temperature and atmospheric pressure. Before each time of electrochemical NRR test, the cathode chamber was purged with Ar or N<sub>2</sub> at the

flow rate of 50 mL min-1 for 30 min.

#### 4. Cathode preparation

Typically, 10 mg catalyst and 20  $\mu$ L of 5 wt% Nafion solution were mixed with 980  $\mu$ L ethanol by sonication for 30 min to form a homogeneous ink. Then, 10  $\mu$ L electrocatalytic ink was coated on carbon paper (1×1 cm<sup>2</sup>) using spray gun. The loading of the catalyst was 0.1 mg cm<sup>-</sup><sup>2</sup>.

#### 5. Determination of ammonia and hydrazine

The concentration of produced NH<sub>3</sub> was determined by indophenol blue method with UV-Vis absorption spectrophotometry. In detail, 2 mL reacted electrolyte obtained from the cathode chamber was mixed with 2 mL of 1 M NaOH solution containing 5 wt% salicylic acid and 5 wt% sodium citrate, then 1 mL of 0.05 M sodium hypochlorite and 0.2 mL of sodium nitroferricyanide (1 wt%) successively. Then, the mixture was maintain at 25 °C for 2h. Finally, the absorption spectrum of the above mixed solution were analyzed at a wavelength of 657 nm by UV-Vis spectrophotometer. The absorbance–concentration curve was determined by a series of concentrations (0-2  $\mu$ gmL<sup>-1</sup>) of standard ammonia chloride solution. The concentration of hydrazine in electrolyte was analyzed by Watt and Chrisp method. In detail, the electrolyte (5 mL) was mixed with a color regent (5 mL) containing p-(dimethylamino) benzaldehyde (5.99 g), concentrated HCl (30 mL) and ethanol (300 mL), and then the mixed solution was measured at a wavelength of 458 nm after 20 min at room temperature. The concentration-absorbance curves were calibrated with a suit of concentrations (0-1  $\mu$ g mL<sup>-1</sup>) of the standard hydrazine monohydrate solutions.

#### 6. Determination of Faradaic efficiency (FE) of NH<sub>3</sub> production

The FE of NH<sub>3</sub> production could be calculated by Eq.(2)

$$FE = 3F \times n_{NH_3}/Q$$
<sup>(2)</sup>

in which the faraday constant F is 96485 C mol<sup>-1</sup>, the mole of NH<sub>3</sub> is n<sub>NH3</sub>, the Q is the total charge consumed in the electrolysis process.

#### 7. <sup>15</sup>N<sub>2</sub> isotope labeled experiment

During the catalysis, the pre-purified <sup>15</sup>N<sub>2</sub> gas was kept feeding into the electrolyte. Before the experiment, the H-type cell was well sealed and degassed under vacuum to remove the air. Then, 20 mL <sup>15</sup>N<sub>2</sub> gas was slowly injected into the cell using the syringe every 10 min for 2 h. After electrolysis, the abtained NH4<sup>+</sup>-contained electrolyte was detected by using 1H NMR spectroscopy (Bruker Avance III HD 600 MHz).

#### 8. Computational methods

Plane-wave density functional theory (DFT) calculations were performed on CASTEP code of the Materials Studio package of Accelrys Inc. Generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) functional was employed for the DFT exchange correlation energy and ultrasoft pseudo-potentials are used for the core electrons. A planewave basis set with an energy cut-off energy of 400 eV was assigned and the self-consistent field (SCF) tolerance was  $2 \times 10^{-5}$  eV. The force and energy convergence criterion for atomic relaxation was 0.05 eV Å<sup>-1</sup> and  $2 \times 10^{-6}$  eV atom<sup>-1</sup>, respectively. The graphene (002) surface was modeled by a periodic there-layer slab repeated in 4×4 surface unit cell with a vacuum width of 12 Å between the slabs along the Z axis, where all atoms were fully relaxed. The Brillouin zone was sampled by  $1 \times 1 \times 1$  Monkhorst-Pack mesh k-points for surface calculation. The Gibbs free energy change of each step is calculated as following equation:  $\Delta G = \Delta E + \Delta EZPE - T\Delta S$ , where  $\Delta E$  is the chemisorption energy change between the reactant and product species adsorbed on catalyst surface obtained directly from DFT calculations,  $\Delta EZPE$  is the difference in zero point energy, T is the temperature (T=298.15 K) and  $\Delta S$  is the entropy difference. The value of  $\Delta G$  (0) was calculated based on at the potential of 0 V vs RHE.  $\Delta G(U) = \Delta G(0) + eU$ , where U is the applied potential [1].



Figure S1. N 1s XPS spectra for the catalysts NC-600, 800, 1000.



Figure S2. O 1s XPS spectra for the catalysts NC-600, 800, 1000.



Figure S3. C 1s XPS spectra for the catalysts NC-600, 800, 1000.



Figure S4. Raman spectra for the catalysts NC-600, 800, 1000.



Figure S5. XRD pattern for the catalysts NC-600, 800, 1000.



**Figure S6**. N<sub>2</sub> adsorption-desorption isotherms and the pore size distributions of the prepared catalysts.



Figure S7. N2-TPD profiles of the NC-600, NC-800 and NC-1000 catalysts.

	Elemental analysis		Contrib	oution of N1	BET analysis			
	C N		Pyridinic Pyrrolic		Graphitic	Sbet	Pore volume	
	(wt %)	(wt %)	Ν	Ν	Ν	(m <sup>2</sup> g <sup>-1</sup> )	(cm g-1)	
NC-600	74.99	6.44	35.4	7.1	57.5	307.7	0.166	
NC-800	74.08	3.05	25.7	6.7	67.6	913.7	0.622	
NC-1000	72.76	1.49	19.8	6.6	73.6	623.8	0.407	

Table S1. Chemical composition and texture properties of the catalyst NC-T

Table S2. Chemical composition and NH3 yield and FEs of the catalyst fresh- and used-

NC-800

	NH <sub>3</sub> yield rate	FEs (%)	
Sample	(µg h <sup>-1</sup> mg <sup>-1</sup> cat)		
fresh-NC-800	16.27	27.51	
used-NC-800	16.28	24.43	



**Figure S8**. The photograph of H-cell with three-electrode cell and the working electrode connections of NRR process.

The experimental setup was mainly made up of three parts, including the pretreatment of feeding gas, electrochemical reduction reaction device, and tail gas trap. The pretreatment of feeding gas was used to exclude any possible contamination of NO<sub>x</sub> impurity of the feeding gas (N<sub>2</sub>, Ar), which using glass vessel containing 0.1 M NaOH (50 mL) solution to absorb the impurity. The ambient NRR performance of NC-800 was conducted in a typical H-cell separated by a piece of Nafion membrane in N<sub>2</sub>-saturated HCl (0.1 M) electrolyte. The tail gas trap was used to absorb the possible NH<sub>3</sub> product released from the electrolyte and protect the cathode chamber against pollutions.



**Figure S9**. (a) UV-vis curves of indophenol assays with  $NH_{4^+}$  ions after incubated for 2 h at HCl solution. (b) Concentration-absorbance curve of  $NH_{4^+}$  ions with a serious of standard concentration at HCl solutions



**Figure S10**. UV-vis absorption spectra of the electrolytes stained with an indophenol indicator after NRR electrolysis.



**Figure S11**. (a) UV-vis curves of Watt and Chrisp assays with N<sub>2</sub>H<sub>4</sub> after incubated for 2 h at HCl solution (b) Concentration-absorbance curve of N<sub>2</sub>H<sub>4</sub> solution with a serious of standard concentration at HCl solution.



**Figure S12**. Determination of the formation of by-product N<sub>2</sub>H<sub>4</sub> over the NC-800 at different potential (vs RHE).



**Figure S13**. The NH<sub>3</sub> yield and FEs over the catalysts NC-600, 800 and 1000 at -0.35 eV (vs RHE).



Figure S14. The NH $_3$  yield of the cathode chamber, tail gas trap, and anode chamber over the catalysts NC-800 at -0.35 V.



**Figure S15.** (a) Ion chromatography of a suit of NH<sub>4</sub><sup>+</sup> at HCl solution. (b) Concentration-area curve of NH<sub>4</sub><sup>+</sup> ions with a serious of standard concentration at HCl solutions



**Figure S16.** UV-vis absorption spectra of the electrolytes stained with an indophenol indicator after NRR electrolysis.



**Reaction pathway** 

Figure S17. The Mars-van-Krevelen mechanism for electrochemical nitrogen reduction reaction to

ammonia for NC-800. The free energy profiles and the structures of intermediates are shown in the

reaction path.



**Scheme S1.** a) Side view, and b) top view of the optimized pyridinic-N doped graphitic porous carbon structures along the hydrogenation process. (C-grey sphere, N-blue sphere, H-white sphere)

Density functional theory (DFT) calculations were conducted to investigate the active sites and mechansim of NC-800 in NRR process. The doped pyridinic-N in graphitic carbon was verified to be the active sites in NRR, reported by Wu and Zhao et al. N atoms loacted in the outmost surface layer of the carbon can be readly reduced to NH3 and leave N vacancy on the surface, which are active sites for absorbing gaseous  $N_2$  molecules to continue the successive NRR process. Moreover, compared with the dissociation and association N<sup>2</sup> mechanisms on carbon, the MvK mechanism could realize the NRR at lower overpotentials and less energy input, which beneficial for more efficient NH<sub>3</sub> production. The results of the DFT reveal that two adjacent pyridinic-N vacancy species could absorb the N2 molecule, which can be hydrogenated by the proton H<sup>+</sup>, followed by the process N-N $\rightarrow$ N-NH $\rightarrow$ HN-NH $\rightarrow$ HN-NH<sub>2</sub> $\rightarrow$ HN-NH<sub>3</sub>. After the NH<sub>3</sub> was released from the surface of the carbon, leaving the nitrogen vacancies for further absorption and activation. In detail, the bond lenth of the N-N was 1.49 Å, which is much larger than that of  $N_2$  (1.1 Å) means that the N-N is more active hydrogenation than N<sub>2</sub>. As shown in Scheme S1 and Figure S17, in the first step, the N-N was cleavage and hydro-genation with the first H<sup>+</sup> happens with a free energy of 1.20 eV. Then, the second H<sup>+</sup> was combined with the the other N with -0.66 eV. In the third step, the HN-NH2 was formed by 1.64 eV. Next, HN-NH<sup>3</sup> was formed and the first NH<sup>3</sup> was released from the graphitic carbon, the free energy changes by 0.48 eV and -1.21 eV, respectively. On the basis of the obtained information mentioned above, the mechanism of NC-800 as a active NRR catalyst was proposed as follows: the doped pyridinic-N can be electrocatalytic reduction to NH<sub>3</sub>, thus generating N vacancies in carbon as a active sites for N<sub>2</sub> adsorbtion, activation and hydrogenation. Meanwhile, the formed N vacanies also result in forming the unsaturated coordinated carbon. Though, the unsaturated carbon does not contribute to the observed NRR catalytic activity, it would likely tune electronic structure of catalyst, then facilitate the NRR process.

Table S3.	The comparable	results of ou	r work and	other 1	recently	reported	carbon-	based	NRR
electrocatalysts.									

Catalyst	Potential(V)	Electrolyte	NH₃ yield rate	FEs (%)	Detection method	Ref.
N-doped biomass carbon	-0.35	0.1 M HCl	16.3 μg h <sup>-1</sup> mg <sup>-1</sup> cat	27.5	indophenol blue method	This work
O-KFCNTs	-0.85/-0.8	0.1 M HCl	25.12 μg h <sup>-1</sup> mg <sup>-1</sup> cat	9.1 (-0.8 V)	indophenol blue method	[2]
			(-0.85 V)			
O-CNT	-0.4	0.1 M LiClO4	32.33 μg h <sup>-1</sup> mg <sup>-1</sup> cat	12.5	indophenol blue method	[3]
Fe-N/C	-0.2	0.1 M KOH	34.83 μg h <sup>-1</sup> mg <sup>-1</sup> cat	9.28	Nessler's reagent method	[4]
NPC	-0.4	0.005 M	22.27 $\mu$ g h <sup>-1</sup> mg <sup>-1</sup> <sub>cat</sub>	9.98	indophenol blue method	[5]
		H2SO4				
Au6/Ni	-0.14	0.05 M H2SO4	$7.4 \ \mu g \ h^{-1} m g^{-1}{}_{cat}$	67.8	Nessler's reagent method	[6]
BP@SnO2-x	-0.4	0.1 M Na2SO4	48.87 μg h <sup>-1</sup> mg <sup>-1</sup> cat	14.6	Nessler's reagent method	[7]
Fe3C@C	-0.2	0.05 M H2SO4	8.53 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat</sub>	9.15	indophenol blue method	[8]
NC-Cu-SA	-0.3	0.1 M HCl	49.3 µg h <sup>-1</sup> mg <sup>-1</sup> cat	11.7	indophenol blue method	[9]
BNS	-0.8	0.1 M Na2SO4	13.22 μg h <sup>-1</sup> mg <sup>-1</sup> cat	4.04	indophenol blue method	[10]
LiMn2O4 NF	-0.5	0.1 M HCl	15.83 µg h <sup>-1</sup> mg <sup>-1</sup> cat	7.44	indophenol blue method	[11]
TiO2/Ti3C2Tx	-0.55/-0.45	0.1M HCl	32.17 $\mu$ g h <sup>-1</sup> mg <sup>-1</sup> <sub>cat</sub>	16.07	indophenol blue method	[12]
			(-0.55V)	(-0.45V)		
O-NC	-0.6	0.1M HCl	20.15 μg h <sup>-1</sup> mg <sup>-1</sup> cat	4.97	indophenol blue method	[13]
NCM-Au	-0.2/-0.1	0.1M HCl	0.36g m <sup>-2</sup> h <sup>-1</sup>	22	indophenol blue method	[14]
			(-0.2V)	(-0.1V)		

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