## **Supporting Information**

# Multi-yolk-shell Bismuth@Porous Carbon as a Highly Efficient Electrocatalyst for Artificial N<sub>2</sub> Fixation under Ambient Conditions

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### <sup>15</sup>N<sub>2</sub> Isotope Labeling Experiments

An isotopic labeling experiment used  ${}^{15}N_2$  (98 atom %  ${}^{15}N$ ) as the feed gas to clarify the source of ammonia. Before starting the test, labelled  ${}^{15}N_2$  gas was pre-purified through flowing into alkaline solution (pH=13 KOH aqueous solution) and acid solution (pH=1 H<sub>2</sub>SO<sub>4</sub> aqueous solution) to remove any N contamination in containing  ${}^{15}N_2$  solution. In the electrocatalytic N<sub>2</sub> reduction experiment, Argon gas was purged to the cathodic cell to remove impurity and then purging for 30 min with the gas. After  ${}^{15}N_2$  electroreduction for 2 h at -0.4 V (vs. RHE) in a 0.1 M HCl solution, 50 mL of the electrolyte was taken out and concentrated to 1 mL. Afterwards, 0.5 mL of the resulting solution was taken out and mixed with 0.05 mL d6-DMSO for  ${}^{1}$ H nuclear magnetic resonance (NMR, 600MHz) measurement. Similarly, the amount of  ${}^{14}NH_4^+$  was quantitatively determined by this method when  ${}^{14}N_2$  (ultra-high-grade purity, 99.999%) was the feed gas.

#### **Computational Details**

All the calculations were performed using the plane wave-based density functional theory (DFT) based code VASP. [1] The basis sets with energy cutoff of 450 eV were used for our calculations. The projector-augmented wave (PAW) [2] with the generalized gradient approximation (GGA) refined by Perdew, Burke and Ernzerhof (PBE) [3] was used to describe the interaction between nuclei-electron and electron-electrons. An energy convergence of  $1 \times 10^{-5}$  eV was set to abort SCF process and a residue force less than 0.02 eV Å<sup>-1</sup> was used for geometric optimization process. NRR processes on Bi (012), Bi (104), and Bi (110) were investigated and the vacuum layer was set as 15 Å in order to

eliminate the interactions between layers and their neighboring layers. Bi (012), Bi (104) and Bi (110) were modelled by four-layer (2×2) supercells. During the geometric optimization processes, the bottom two layers of all the structures are fixed at their bulk position. While, only adsorbed surface species are relaxed to calculate the vibrational frequency required for zero-point energy (ZPE) correction and the calculation of vibrational entropy. The Monkhorst–Pack grids of  $4 \times 4 \times 1$ ,  $3 \times 4 \times 1$  and  $3 \times 3 \times 1$  were adopted for Bi (012), Bi (104) and Bi (110) surfaces, respectively.

The reaction Gibbs free energy ( $\Delta G$ ) of each elementary steps along NRR processes were obtained by  $\Delta G = \Delta E + \Delta ZPE -T\Delta S + \Delta G_{pH} + \Delta G_{U}$ , where  $\Delta E$  is the reaction energy difference between the product and reactant directly obtained from DFT calculations,  $\Delta ZPE$  and  $\Delta S$  are the change in zero point energies and entropy at 298.15 K (T = 298.15 K),  $\Delta G_{pH}$  is the free energy correction of pH, which can be calculated by  $\Delta G_{pH} = k_BT \times pH \times 2.303$ , and the pH value was set to be zero in this work.  $\Delta G_U$  is the free energy contribution related to electrode potential U.

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Figure S1. SEM image of (a) MB@PC-600 and (b) MB@PC-800



Figure S2. (a-c) TEM images taken of MB@PC-600, (d-f) EDX elemental mapping images of MB@PC-600.



Figure S3. (a-c) TEM images taken of MB@PC-800, (d-f) EDX elemental mapping images of MB@PC-800.



Figure S4. XPS survey spectra of MB@PC-600, MB@PC-700 and MB@PC-800.



**Figure S5.** XPS spectrum for MB@PC-700 in the C 1s region.



Figure S6. N<sub>2</sub>-TPD curve of MB@PC-700.



Figure S7. Image of the apparatus for NRR measurement.



**Figure S8.** UV-Vis absorption curves of various concentrations of  $NH_3$  stained with indophenol indicator and incubated for 2 h at room temperature; (b) calibration curve used for calculation of  $NH_3$  concentrations; (c) the chromogenic reaction of indophenol indicator with  $NH_3$ .



Figure S9. LSV curves of MB@PC-600, MB@PC-700, MB@PC-800 and carbon paper in  $N_2$  saturated 0.1 M HCl solution.



Figure S10. (a) UV-Vis absorption spectra of electrolytes stained with indophenol indicator after NRR electrolysis for MB@PC-T (T refers different temperatures, such as 600, 700 and 800 °C) at -0.5 V for 2 h at N<sub>2</sub> atmosphere; (b) Corresponding NH<sub>3</sub> yields and FEs of MB@PC-T.



**Figure S11.** Electrochemically active surface area measurement.  $(a_1-d_1)$  Cyclic voltammograms of different samples at various scan rates from 10 to 110 mV s<sup>-1</sup> in the potential range between -0.02 and -0.12 V;  $(a_2-d_2)$  The capacitive current density difference at -0.07 V plotted & scan rate for different catalysts.



Figure S12. Electrochemical impedance spectra of MB@PC-600, MB@PC-700, MB@PC-800 and carbon paper at -0.5 V in  $N_2$  saturated 0.1 M HCl.



**Figure S13.** (a) UV-vis absorption spectra of the electrolytes stained with indophenol indicator after electrolysis under various conditions (N<sub>2</sub>-saturated and Ar-saturated over MB@PC-700/CP at -0.50 V for 2 h; open circuit potential in N<sub>2</sub>-saturated solution over MB@PC-700/CP for 2 h; carbon paper in N<sub>2</sub>-saturated solution at -0.50 V for 2 h ). (b) Corresponding NH3 yields of MB@PC-700/CP and carbon paper (carbon paper mass: 8 mg), respectively.



Figure S14. (a) UV-Vis curves of various concentrations of  $N_2H_4$  stained with p-C<sub>9</sub>H<sub>11</sub>NO indicator and incubated for 20 min at room temperature. (b) Calibration curve used to calculate the concentrations of  $N_2H_4$ . (c) the chromogenic reaction of p-C<sub>9</sub>H<sub>11</sub>NO indicator with  $N_2H_4$ .



Figure S15. UV-Vis absorption spectra of the electrolytes stained with  $p-C_9H_{11}NO$  indicator after 2h electrolysis using MB@PC-700 at a series of potentials (-0.3 to -0.7V).



Figure S16. (a) Chronoamperometry curves and (b) UV-Vis absorption curves of MB@PC-700 at -

0.5 V for 8 cycles.



Figure S17: Stability test for MB@PC-700 during repeated NRR processes at -0.5 V



Figure S18. Long-term chronoamperometry curve of MB@PC-700 catalysts at -0.5 V.



Figure S19: the XPS pattern of MB@PC-700 catalyst before and after long-term NRR testing , (a)

survey, (b) Bi 4f, (c) C1s.



**Figure S20**: Free energy diagram of  $N_2$  hydrogenation via alternating pathway on Bi (012) (a), Bi (104) (b) and Bi (110) (c) surface. Blue dashed lines show the hydrogenation processes from NHNH.



Figure S21: Minimum energy pathways of the hydrogenation of N<sub>2</sub> into NHNH via N<sub>2</sub>+2\*H $\rightarrow$  NHNH on Bi(104) (a) and Bi(110) (b)surface.



**Figure S22**: Work function diagram of Bi (012), Bi (104), Bi(110) surfaces and graphene represented graphite based carbon material.

Catalysts	Electrolyte	NH <sub>3</sub> yield FE		Reference
MB@PC-700	0.1 M HCl	$28.63 \ \mu g \cdot h^{-1} \cdot mg^{-1}{}_{cat}.$	10.58	This work
Bi <sub>4</sub> V <sub>2</sub> O <sub>11</sub> /CeO <sub>2</sub>	0.1 M HCl	23.21 $\mu$ g · h <sup>-1</sup> · mg <sup>-1</sup> <sub>cat</sub> .	10.16	S1
Bi NS/CF	0.1 M HCl	5.26 $\mu$ g · h <sup>-1</sup> · mg <sup>-1</sup> <sub>cat</sub> .	10.26	S2
Bi NS	0.1 M Na <sub>2</sub> SO <sub>4</sub> 13.23 $\mu$ g · h <sup>-1</sup> · mg <sup>-1</sup> <sub>cat</sub>		10.49	S3
β-Bi <sub>2</sub> O <sub>3</sub> nanoflower	0.1 M Na <sub>2</sub> SO <sub>4</sub>	19.92 $\mu$ g · h <sup>-1</sup> · mg <sup>-1</sup> <sub>cat</sub> .	4.3	S4
defect-rich Bi nanoplates	0.2 M Na <sub>2</sub> SO <sub>4</sub>	.2 M Na <sub>2</sub> SO <sub>4</sub> 5.453 $\mu$ g · h <sup>-1</sup> · mg <sup>-1</sup> <sub>cat</sub> .		S5
MBN	0.1 M Na <sub>2</sub> SO <sub>4</sub>	18.2 $\mu$ g · h <sup>-1</sup> · mg <sup>-1</sup> <sub>cat</sub> .	5.5	S6
MoS <sub>2</sub> –rGO	0.1 M LiClO <sub>4</sub>	24.82 $\mu$ g · h <sup>-1</sup> · mg <sup>-1</sup> <sub>cat</sub> .	4.58	S7
TiO <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub> Tx	0.1 M HCl	$26.32 \ \mu g \cdot h^{-1} \cdot mg^{-1}_{cat}.$	8.42	S8
O-KFCNTs	0.1 M HCl	$25.12 \ \mu g \cdot h^{-1} \cdot mg^{-1}_{cat}.$	5.7	S9
Ti <sub>3</sub> C <sub>2</sub> Tx nanosheet	0.1 M HCl	$20.4 \ \mu g \cdot h^{-1} \cdot mg^{-1}_{cat}.$	9.3	S10
N-doped porous carbon	0.05 M H <sub>2</sub> SO <sub>4</sub>	$23.8 \ \mu g \cdot h^{-1} \cdot mg^{-1}_{cat}.$	1.4	S11
O-CN/CP	0.1 M HCl	$20.15 \ \mu g \cdot h^{-1} \cdot mg^{-1}_{cat}.$	4.97	S12
NPC	0.1 M HCl	$23.8 \ \mu g \cdot h^{-1} \cdot mg^{-1}_{cat}.$	1.42	S13
MoO <sub>3</sub>	0.1 M HCl	29.43 $\mu$ g · h <sup>-1</sup> · mg <sup>-1</sup> <sub>cat</sub> .	1.9	S14
N-doped carbon	0.1 M HCl	$15.7 \ \mu g \cdot h^{-1} \cdot mg^{-1}_{cat}$	1.45	S15

Table S1. Summary of the representative reports on electrocatalytic  $N_2$  fixation under ambient conditions

PCN	0.1 M HCl	8.09 $\mu$ g · h <sup>-1</sup> · mg <sup>-1</sup> <sub>cat</sub> .	11.59	S16
Au-TiO <sub>2</sub>	0.1 M HCl	$21.4 \ \mu g \cdot h^{-1} \cdot mg^{-1}_{cat}.$	8.11	S17
α-Au/CeOx-RGO	0.1 M HCl	8.31 $\mu$ g · h <sup>-1</sup> · mg <sup>-1</sup> <sub>cat</sub> .	10.1	S18
Ru NPs	0.01 M HCl	21.4 $\mu$ g · h <sup>-1</sup> · mg <sup>-1</sup> <sub>cat</sub> .	5.4	S19

**Table S2:** The Gibbs free energy of the hydrogenation of N<sub>2</sub> to \*NNH ( $\Delta G_{*NNH}$ ), the adsorption free energy ( $\Delta G_{*H}$ ) of atomic hydrogen and the energy barrier of N<sub>2</sub> hydrogenation (E<sub>a,NHNH</sub> )to NHNH on neutral and positively charged Bi(012), Bi(104) and Bi(110) surfaces.

Bi	(012)	(012)+	(104)	(104)+	(110	(110)
					)	+
$\Delta G_{*_{NNH}}(eV)$	2.62	2.20	1.88	1.87	2.00	2.10
)						
$\Delta G_{*H}(eV)$	0.81	0.76	0.57	0.62	0.64	0.67
E <sub>a,NHNH</sub> (eV)	0.71	0.70	1.18	1.20	1.29	1.28

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