Electronic Supplementary Information

Experimental section

Materials: Amorphous boron (B), red phosphorus (P), sodium citrate dehydrate (C₆H₅Na₃O₇·2H₂O), nitroferricyanide (III) dihydrate (Na₂Fe(CN)₅NO·2H₂O), and Nafion (5wt%) sodium were purchased from Aladdin Ltd. in Shanghai. Para-(dimethylamino) benzaldehyde (C₉H₁₁NO), salicylic acid (C₇H₅O₃), sodium citrate dehydrate (C₆H₅Na₃O₇·2H₂O), hydrazine hydrate (N₂H₄·H₂O), sodium hypochlorite (NaClO), sodium hydroxide (NaOH), hydrochloric acid (HCl), ethanol (CH₃CH₂OH), and carbon paper were bought from Beijing Chemical Corporation. The ultrapure water was purified through a Millipore system used throughout all experiments.

Preparation of BP: BP was synthesis through a vacuum-seal strategy. A total weight of 200 mg elements mixture which the molar ratio of B:P was 1:1.2. After vacuum sealing, the silica tube was annealing at 1200 °C in a muffle furnace for 10 h. The BP was prepared well. Moreover, B catalyst was prepared by the same preparation without the presence of P.

Preparation of BP/CP: Carbon paper (CP) was cleaned via brief sonication with ethanol and water for several times. To prepare the BP/CP, 10 mg BP and 40 µL 5 wt% Nafion solution were dispersed in 960 µL water/ethanol (V : V = 1 : 3) followed by 1-h sonication to form a homogeneous ink. 20 µL ink was loaded onto a CP (1 × 1 cm²) and dried under ambient condition. The BP/CP working electrode was prepared well.

Characterizations: TEM images were collected on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) operated at 200 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. The absorbance data of spectrophotometer were acquired on SHIMADZU UV-1800 UV-Vis spectrophotometer.

Electrochemical measurements: The N₂ reduction experiments were carried out in a two-compartment cell under ambient condition, which was separated by Nafion 117 membrane. The membrane was treated in H₂O₂ (5%) aqueous solution at 80 °C for 1 h and dipped in 0.1 M H₂SO₄ at 80 °C for another 1 h. And finally, the membrane was treated in ultrapure water at 80 °C for 6 h. The electrochemical measurements were conducted on a CHI660E electrochemical analyzer (CH Instruments, China) in a typical three-electrode setup with an electrolyte solution of 0.1 M HCl (30 mL), a graphite rod
and Ag/AgCl (filled with saturated KCl solution) as the counter and reference electrode, respectively. The potentials reported in this work were converted to RHE scale via calibration with the following equation: $E_{\text{vs RHE}} = E_{\text{vs Ag/AgCl}} + 0.197 + 0.059 \times \text{pH}$. For N$_2$ reduction experiments, the electrolyte was bubbled with N$_2$ for 30 min before the measurement.

**Determination of NH$_3$:** Concentration of produced NH$_3$ was spectrophotometrically determined by spectrophotometry measurement with salicylic acid.$^1$ In detail, 2 ml aliquot of solution was removed from the cathodic chamber, and then added into 2 ml 1.0 M NaOH solution containing C$_7$H$_6$O$_3$ and C$_6$H$_5$Na$_3$O$_7$·2H$_2$O (5 wt%), then added 1 ml NaClO (0.05 M) and 0.2 ml Na$_2$[Fe(NO)(CN)$_5$].2H$_2$O (1 wt%) aqueous solution in turn. After standing at room temperature for 2 hours, the UV-Vis absorption spectrum was measured. The concentration of indophenol blue was determined using the absorbance at a wavelength of 655 nm. The concentration-absorbance curves were calibrated using standard NH$_4$Cl solution with a series of concentrations. The fitting curve ($y = 0.329x + 0.043$, $R^2$=0.999) shows good linear relation of absorbance value with NH$_3$ concentration by three times independent calibrations.

**Determination of N$_2$H$_4$:** The N$_2$H$_4$ presented in the electrolyte was estimated by the method of Watt and Chrisp.$^2$ A mixed solution of C$_9$H$_{11}$NO (5.99 g), HCl (concentrated, 30 mL) and ethanol (300 mL) was used as a color reagent. Typically, 5 mL electrolyte was removed from the cathodic chamber, after that, added into 5 mL above prepared color reagent and stirring 10 min at room temperature. The absorbance of the resulting solution was measured at 455 nm. The concentration absorbance curves were calibrated using standard N$_2$H$_4$ solution with a series of concentrations. The fitting curve shows good linear relation of the absorbance with N$_2$H$_4$ concentration ($y = 0.397x + 0.038$, $R^2 = 0.999$).

**Determination of NH$_3$ yield and FE:** The Faradic efficiency (FE) for N$_2$ reduction was defined 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 was measured using colorimetric methods. NH$_3$ yield was calculated using the following equation:

$$\text{NH}_3 \text{ yield} = \frac{[\text{NH}_3] \times V}{(\text{m}_{\text{cat.}} \times t)}$$

Assuming three electrons were needed to produce one NH$_3$ molecule, the FE could be calculated as follows:
\[ FE = 3 \times F \times [\text{NH}_3] \times V / (17 \times Q) \times 100\% \]

Where \( F \) is the Faraday constant, \([\text{NH}_3]\) is the measured \( \text{NH}_3 \) concentration, \( V \) is the volume of the electrolyte in the cathodic chamber, \( Q \) is the total quantity of applied electricity; \( t \) is the reduction time; \( m_{\text{cat.}} \) is the loaded mass of catalyst on carbon paper.

**Computational details:** Spin-polarized density functional theory (DFT) calculations were performed by using the plane wave-based Vienna ab initio simulation package (VASP). The generalized gradient approximation method with Perdew-Burke-Ernzerhof (PBE) functional was used to describe the exchange-correlation interaction among electrons. The van der Waals (vdW) correction with the Grimme approach (DFT-D3) was included in the interaction between single molecule/atoms and substrates. The energy cutoff for the plane wave-basis expansion was set to 500 eV and the atomic relaxation was continued until the forces acting on atoms were smaller than 0.01 eV Å\(^{-1}\). The BP (111) and (200) surfaces was modeled using a 3 \times 2 slab with four layers (B−P) which the bottom layer is fixed, and are separated by 15 Å of vacuum. The Brillouin zone was sampled with 2 \times 2 \times 1 Gamma-center k-point mesh, and the electronic states were smeared using the Fermi scheme with a broadening width of 0.1 eV.

The free energies of the reaction intermediates were obtained by \( \Delta G = \Delta E_{\text{ads}} + \Delta ZPE - T\Delta S + \Delta G(U) + \Delta G(pH) \), where \( \Delta E_{\text{ads}} \) is the adsorption energy, \( ZPE \) is the zero point energy and \( S \) is the entropy at 298 K. The effect of a bias was included in calculating the free energy change of elementary reactions involving transfer of electrons by adding \( \Delta G(U) = -n e U \), where \( n \) is number of electrons transferred and \( U \) is the electrode potential. In our calculations, we used \( U = -0.60 \text{ V (vs. RHE)} \). \( \Delta G(pH) = -k_B T \ln 10 \times pH \), where \( k_B \) is the Boltzmann constant, and \( pH = 1 \) for electrolyte. In this study, the entropies of molecules in the gas phase are obtained from the literature.
Fig. S1. XPS survey spectrum for BP.
Fig. S2. (a) UV-Vis absorption spectra of indophenol assays with NH$_3$ concentrations after incubated for 1 h at room temperature in 0.1 HCl. (b) Calibration curve used for calculation of NH$_3$ concentrations in 0.1 HCl.
Fig. S3. (a) UV-Vis absorption spectra of N$_2$H$_4$ concentrations after incubated for 10 min at room temperature. (b) Calibration curve used for calculation of N$_2$H$_4$ concentrations.
Fig. S4. (a) UV-Vis absorption spectra of indophenol assays with NH$_3$ concentrations after incubated for 1 h at room temperature in 0.1 M Na$_2$SO$_4$. (b) Calibration curve used for calculation of NH$_3$ concentrations in 0.1 M Na$_2$SO$_4$. (c) Time-dependent current density curves over at –0.60 V for 2 h using BP/CP in 0.1 M Na$_2$SO$_4$. (d) NH$_3$ yields and FEs for BP/CP at –0.60 V in 0.1 M Na$_2$SO$_4$ and 0.1 M HCl.
**Fig. S5.** NH₃ yields and FEs for BP/CP at –0.60 V with different loadings.
Fig. S6. UV-Vis absorption spectra of electrolytes stained with para-(dimethylamino) benzaldehyde indicator before and after 2 h electrolysis at –0.60 V.
Fig. S7. UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after 2 h electrolysis at $-0.60$ V under different electrochemical conditions.
Fig. S8. (a) Time-dependent current density curves over at −0.60 V for 2 h using BP/CP after 24-h electrolysis. (b) UV-Vis absorption spectra of the electrolytes colored with indophenol indicator in no-light environment for 2 h.
Fig. S9. XRD pattern of BP after stability test.
TEM image of BP nanoparticles after stability test.
Fig. S11. XPS spectra of BP in the (a) B 1s and (b) P 2p regions after stability test.
Fig. S12. DOS of B active site before and after N$_2$ adsorption in BP (111) surface.
Fig. S13. Atom configurations for NRR on B (111) surface.
Fig. S14. Free energy diagram of NRR on BP (200) surface at –0.60 V.

Reaction Pathways

$U = -0.60 \, \text{V}$

$pH = 1$
Fig. S15. Atom configurations for NRR on B (200) surface.
Fig. S16. HER on BP (111) and (200) surfaces.
Fig. S17. Densities of active site on (a) elementary B and (b) BP. The cross represents active site.
Table S1. Comparison of the catalytic performances of non-metal NRR electrocatalysts at ambient conditions in aqueous electrolytes.

<table>
<thead>
<tr>
<th>Testing method</th>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>NH$_3$ yield</th>
<th>FE(%)</th>
<th>Ref.</th>
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<td></td>
<td>BP nanoparticles</td>
<td>0.1 M HCl</td>
<td>26.42 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>12.7</td>
<td>This work</td>
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<td>boron nanosheet</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>13.22 µg h$^{-1}$ mg$^{-1}$ cat.</td>
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<td></td>
<td>boron nanosheet</td>
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<td>3.12 µg h$^{-1}$ mg$^{-1}$ cat.</td>
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<td>defect-rich fluorographene</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>9.3 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>4.2</td>
<td>10</td>
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<td>BN</td>
<td>0.1 M HCl</td>
<td>22.4 µg h$^{-1}$ mg$^{-1}$ cat.</td>
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<td>oxygen-doped carbon nanosheet</td>
<td>0.1 M HCl</td>
<td>20.15 µg h$^{-1}$ mg$^{-1}$ cat.</td>
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<td>black P nanosheets</td>
<td>0.01 M HCl</td>
<td>31.37 µg h$^{-1}$ mg$^{-1}$ cat.</td>
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<td>PTCA–rGO</td>
<td>0.1 M HCl</td>
<td>24.7 µg h$^{-1}$ mg$^{-1}$ cat.</td>
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<td>sulfur dots-graphene nanohybrid</td>
<td>0.5 M LiClO$_4$</td>
<td>28.56 µg h$^{-1}$ mg$^{-1}$ cat.</td>
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<td>S-doped carbon nanosphere</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>19.07 µg h$^{-1}$ mg$^{-1}$ cat.</td>
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<td>oxygen-doped hollow carbon microtubes</td>
<td>0.1 M HCl</td>
<td>25.12 µg h$^{-1}$ mg$^{-1}$ cat.</td>
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<td>NPC</td>
<td>0.005 M H$_2$SO$_4$</td>
<td>1.31 mmol h$^{-1}$ g$^{-1}$ cat.</td>
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<td>B-doped graphene</td>
<td>0.05 M H$_2$SO$_4$</td>
<td>9.8 µg h$^{-1}$ cm$^{-2}$</td>
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<td>27.3 µg h$^{-1}$ cm$^{-2}$</td>
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<td>PCN</td>
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<td>B$_4$C</td>
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<td>Nessle’ reagent</td>
<td>N-doped porous carbon</td>
<td>23.8 µg h$^{-1}$ mg$^{-1}$ cat.</td>
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<td>EPA Standard Method</td>
<td>CNS</td>
<td>0.25 M LiClO$_4$</td>
<td>97.18 µg h$^{-1}$ cm$^{-2}$</td>
<td>11.56</td>
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Indophenol blue method
References


