Supporting Information

Constructing Interfacial Boron-Nitrogen Moieties in Turbostratic Carbon for Electrochemical Hydrogen Peroxide Production

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Methods

Material: 1-Methylimidazol (≥99%, purified by redistillation), dichloromethane (99.9% by GC), 5% Nafion were purchased from Sigma-Aldrich, 1-iodobutane (99%) and chloroform-d (99.8% D) were bought from Aldrich, toluene (99.7% by GC) was bought from Honeywell, sodium borohydride (99%) and dicyandiamide (DCDA, 99.5%) were purchased from Acros Organics.

Synthesis of 1-Butyl-3-methylimidazol-2-ylidene borane (ZIL): The synthesis of zwitterionic liquid, 1-butyl-methyl-imidazol-2-ylidene borane, was carried out according to the procedure stated in ref [1].

In a typical synthesis, 16 ml 1-methylimidazole (0.2 mol) and 60 ml dichloromethane were placed in 500 ml round bottom flask, and 27.415 ml iodobutane (0.24 mol, 1.2 eq.) was added with a dropping funnel while the mixture was stirred. The mixture was heated to 50 °C and refluxed overnight. On the next day, the reaction mixture was checked by NMR-spectroscopy until there was no imidazole peak, and then the solvent was removed in vacuum. The crude product (56.94 g) of 1-Butyl-3-methylimidazolium iodide (IL-H-I) was used for further reactions.

Then 56.94 g (0.214 mol) of IL-H-I was dispersed in 200 ml toluene. 9.71 g (0.257 mol, 1.2 eq.) sodium borohydride was added to the mixture, and the mixture was heated to 105 °C and stirred overnight. On the following day, the hot toluene phase was decanted. The other phase was washed twice with hot toluene (105 °C) and decanted again. The collected toluene phase was retained for one day until some solid precipitation of residual sodium borohydride appeared, and then filtered. The toluene was removed by rotary evaporation, and the crude product was dissolved in dichloromethane to further precipitate sodium borohydride and other solid impurities. After filtration, the
dichloromethane was removed in vacuum. 26.74 g of 1-Butyl-3-methylimidazol-2-ylidene borane (ZIL) product was obtained as a transparent liquid.

Synthesis of CNB-ZILs: ZIL and DCDA (in a weight ratio of 1:40) were mixed by ball milling, and the mixture was heated continuously for 4 h to 600 °C in the inert N₂ atmosphere for 2 h. Then it was heated for another 2 h to 800 °C (or 3 h to 900 °C, 4 h to 1000 °C) for 1 h. After cooling down to room temperature, the black free-standing turbostratic carbon product was obtained. All samples are referred to as CNB-ZIL X, where X stands for the preparation temperature. For comparison, pure nitrogen-doped carbon (NC) was also synthesized by heating a mixture of D(-)-Fructose and DCDA (in a weight ratio of 1:40) through the same method.

Structural and electronic property characterization: X-ray diffraction (XRD) measurements were carried out on a Bruker D8 Advance instrument with Cu-Kα radiation. Transmission electron microscopy (TEM) was performed on a Phillips/CM 200 microscope operated at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) was carried out on FEI Nova NanoSEM 450 instrument. High angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray (EDX) mapping were obtained on a spherical aberration corrected transmission electron microscope (JEOL JEM-ARM200F STEM system) which was operated at 200 kV. Electron energy loss (EELS) spectra was observed on a double-Cs-corrected JEOL ARM 200F instrument operated at 200 kV. Fourier transformed infrared (FTIR) spectra were recorded by a Varian 600 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo ESCALAB 250Xi X-ray Photoelectron Spectrometer. Ultraviolet Photoelectron Spectroscopy (UPS) was collected with a He I (21.2 eV) radiation source. The Fermi level of gold reference was used to calibrate the system. CNB-ZIL samples were used as synthesized as described above and pressed into indium foil for the near-edge X-ray absorption fine structure (NEXAFS) experiment. N K-edge, B K-edge and C K-edge NEXAFS spectroscopy measurements were collected at a 55° angle of incidence in a vacuum chamber with a base pressure of 10⁻⁷ mbar on the soft X-ray beamline at the Australian Synchrotron, ANSTO. The signals were acquired in total
electron yield (TEY) mode and the data were processed using the program called QANT.\textsuperscript{[3]} Pore structure properties of the materials were measured via nitrogen adsorption and desorption at 77 K using a volumetric technique on a Quantachrome Quadrasorb SI porosimeter. Prior to analysis, the samples were degassed under vacuum at 150 °C for 20 h.

Electrochemical measurements: The electrochemical measurements were performed in 0.1 M KOH aqueous solution using a three-electrode system on a CHI 760E electrochemical workstation (CH Instruments) assisted with rotation equipment (ALS, Japan) at room temperature. Prior to tests, a homogeneous catalyst ink was prepared by dispersing 5 mg of the catalyst and 25 μL of Nafion solution (5%) into 1 mL ethanol solution, followed by a sonication process for 30 min. The as-obtained ink was then drop-cast onto the polished working electrode with a fixed mass loading of 0.125 mg cm\textsuperscript{-2}. The catalyst-mounted rotating ring-disk electrode (RRDE, glassy carbon, diameter: 4 mm with a Pt ring) was directly used as working electrode for ORR evaluation. Graphite rod and saturated calomel electrode (SCE) were employed as counter and reference electrodes, respectively. All of the obtained potentials were calibrated to a reversible hydrogen electrode (RHE, \(E_{RHE} = E_{SCE} + 0.2415 + 0.059 \times \text{pH}\)) and all current densities were normalized to a geometric surface area. Linear sweep voltammetry for ORR was conducted at a scan rate of 5 mV·s\textsuperscript{-1} without any iR correction. The Tafel slope was calculated using the Tafel equation: \(\eta = b \log \left( \frac{j}{j_0} \right)\) (\(\eta\), \(b\), \(j\) and \(j_0\) represent the overpotential, Tafel slope, current density and exchange current density respectively), and a scan rate of 1 mV s\textsuperscript{-1} was used to obtain the polarization curves for Tafel plots. Long-term ORR stability tests on CNB-ZIL 8 was carried out under an operating potential of 0.3 V vs. RHE.

HO\textsuperscript{2-} selectivity (or molar selectivity) of the catalysts was calculated from the current of both disc and ring electrodes using the following equation:

\[
\text{HO}_2^- \%(\%) = 200 \times \frac{I_r}{N(I_d + I_r)}
\]

where \(I_d\) is disk current, \(I_r\) is ring current, and \(N\) is current collection efficiency of the Pt ring. \(N\) was determined to be 0.32 in our system after calibration using the reversible \([\text{Fe(CN)}_6]^{4-3}\) redox couple (+0.36 vs. SHE). A potential of 1.2 V vs. RHE was applied on the Pt ring of the working electrode at a speed of 1600 r.p.m. during the entire testing process.
The evaluation of Faradaic efficiency (FE) and bulk electrolysis experiments were conducted in a two-compartment cell with Nafion membrane as separator. Both the cathode compartment (35 mL) and anode compartment were filled with 0.1 M KOH aqueous solution. Oxygen was continuously purged into the cathode (working) compartment under vigorous stirring. A graphite rod and a saturated calomel electrode were used as counter and reference electrode respectively. A hydrophobic carbon fiber paper (CFP) loaded with as-prepared CNB-ZIL 8 catalyst (0.25 mg cm\(^{-2}\)) was used as the working electrode. To quantify the amount of HO\(_2^+\) produced, permanganate titration method was employed. Typically, samples with a volume of 1 mL collected at certain time intervals under a specific operation voltage were diluted into 5 mL with 0.05 M H\(_2\)SO\(_4\) and titrated with 0.005 M KMnO\(_4\) aqueous solution. The concentration of HO\(_2^+\) produced was calculated according to the following equation:

\[
C_{\text{HO}_2^-} = \frac{5C_{\text{KMnO}_4} \times V_{\text{KMnO}_4}}{2V_{\text{HO}_2^-}}
\]

where \(C_{\text{HO}_2^-}\) is the HO\(_2^+\) concentration (mol L\(^{-1}\)), \(C_{\text{KMnO}_4}\) is the precise concentration of KMnO\(_4\) solution (mol L\(^{-1}\)), \(V_{\text{KMnO}_4}\) is the volume of KMnO\(_4\) solution consumed during titration (mL), \(V_{\text{HO}_2^-}\) is the volume of HO\(_2^+\) solution.

The cell performance of CNB-ZIL 8-loaded CFP electrode was carried out in a commercially available Micro flow cell (MFC Electrocell North America). This flow reactor comprises a cathode and an anode with three chambers (two liquid chambers and one feeding gas chamber). On the anode side, a dimensionally stable anode (iridium/ruthenium-coated titanium mesh, 10 cm\(^2\) geo) was served as the oxygen evolution reaction (OER) electrode installed on the anode chamber, in close contact with NafionTM 117 membrane to minimise the ohmic resistance loss during operation (~3.2 Ohmics was recorded if around 1 cm distance between anode and membrane). 0.1 M KOH solution was circulated through the anode chamber during operation (50 mL h\(^{-1}\)). As for the cathode part, CNB-ZIL 8-loaded CFP electrode (1.5 cm\(^2\) geo) was directly used as the cathode sandwiched between the liquid chamber and the gas chamber, with gas (15 mL min\(^{-1}\)) feeding on the non-catalyst side (backside of the electrode) from the gas chamber in a flow by configuration to mitigate the limited dissolvability of O\(_2\). In a similar manner, the fresh electrolytes were pumped into the liquid chamber (with a flow rate of 90 mL h\(^{-1}\)) and flow through the catalyst surface (frontside of the electrode).
Reaction Mechanism:

**ORR:**

It is well established that ORR could proceed through a 2-electron-transfer pathway in alkaline media, that is:

\[
O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \quad (\text{at } pH > 11.6, U_{\text{HO2/HO2-}}^0 = 0.74 \text{ V vs. RHE})
\] (1)

Notably, in some other cases, the ORR could also proceed through a 4-electron-transfer pathway rather than a direct 2e\(^-\) process as mentioned above in alkaline media, producing the hydroxyl anions as the dominate products:

\[
O_2 + 2H_2O + 4e^- \rightarrow OOH^* + H_2O + OH^- + 3e^- \tag{2}
\]

\[
OOH^* + H_2O + OH^- + 3e^- \rightarrow O^* + H_2O + 2OH^- + 2e^- \tag{3}
\]

\[
O^* + H_2O + 2OH^- + 2e^- \rightarrow OH^* + 3OH^- + e^- \tag{4}
\]

\[
OH^* + 3OH^- + e^- \rightarrow 4OH^- \tag{5}
\]

where * represents the surface site. However, this process is not preferred in the electrochemical synthesis of hydrogen peroxide, which could lead to a decreased selectivity toward the desirable peroxide species. Additionally, during the 2e\(^-\) ORR process, another unfavourable side reaction is the further 2e\(^-\) reduction of HO\(_2\)^\(-\) product generated on the surface of electrode, which is:

\[
HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \quad (U_{\text{HO2/OH^-}}^0 = 0.86 \text{ V vs. RHE})
\]
Supplementary Results:

Figure S1. SEM images of CNB-ZIL 8 catalysts. Figure S1a shows a stacked nanoflake structure of CNB-ZIL 8 material on a micrometer scale, while Figure S1b exhibits an interconnected thin nanosheet feature of catalysts under higher magnification.
Figure S2. TEM and STEM images of CNB-ZIL 8 catalysts. A scrambled nanosheet structure was revealed by TEM and STEM characterizations in Figure S2a and b. Figure S2c shows a porous nanostructure on the carbon basal plane of CNB-ZIL catalysts. Further performing the HR-TEM measurements evidence a highly disordered turbostratic carbon structure on CNB-ZIL 8 in Figure S2d, which might be ascribed to the homogeneous doping of B and N heteroatoms into the carbon framework that heavily disturbs its graphitic structure.
Figure S3. FFT image of CNB-ZIL 8. Reduced fast Fourier transform (FFT) pattern derived from a selected area in Figure 2c, suggesting the lack of obvious crystalline phases on CNB-ZIL 8 materials.

Figure S4. XRD patterns of CNB-ZIL catalysts. Notably, no obvious Bragg reflections can be observed in the XRD pattern of CNB-ZIL 8, validating the lack of highly crystalized features in a carbon framework with homogeneous doping of B and N elements.
Figure S5. Pore size distribution of CNB-ZIL 8. It is worth noting that a combination of micro- and meso slit-pores can be observed for CNB-ZIL 8 based on the BJH pore size distribution calculated from the adsorption branch, which could benefit a rapid mass transfer during 2e⁻ ORR process involving multistep adsorption/desorption of reactants/products.
Figure S6. XPS survey scans for CNB-ZIL catalysts.

Figure S7. Schematic illustration of highly isolated BN pairs in the carbon network into more aggregated \( h \)-BN domains under an elevated temperature. The black, green and blue spheres represent carbon, boron and nitrogen atoms, respectively.
Figure S8. The corresponding Tafel plots of kinetic current densities for HO$_2^-$ generation.
Figure S9. RRDE measurements of CNB-ZIL 8, pure boron nitride and NC samples for ORR in O₂-saturated 0.1 M KOH under a rotating speed of 1600 rpm. A scan rate of 5 mV s⁻¹ was adopted throughout the whole tests.

Figure S10. Calculated electron work function of CNB-ZIL catalysts derived from the ultraviolet photoelectron spectroscopy (UPS) measurements.
Figure S11. Raman analysis of CNB-ZIL catalysts. (a) Ex situ Raman spectra of CNB-ZIL catalysts. In situ Raman spectra of (b) CNB-ZIL 8 and (c) CNB-ZIL 9 catalysts. The in situ measurements were conducted in O2-saturated 0.1 M KOH solution.

To eliminate the interference of the structural defects in carbon materials, ex situ and in situ Raman analysis were further conducted on CNB-ZIL catalysts. As shown in Figure S11a, no obvious characteristic peaks belonging to highly crystalized graphitic carbon (e.g. G band at 1597 cm⁻¹) or structural defects (e.g. D band at 1347 cm⁻¹) can be observed in CNB-ZIL 8. This might be due to the highly isolated distribution of B-N pairs in turbostratic carbon that forms a polymer-like B-N-C network without obvious graphitic carbon structure, as also confirmed by XRD measurement (Figure S4). In this regard, no correlation between structural defects and the high 2e⁻ ORR performance on CNB-ZIL 8 can be established. To further exclude the influence of the structural defects on ORR activity of CNB-ZIL 8, in situ Raman characterizations were also performed. It is revealed that no significant changes on Raman spectra (Figure S11b) can be detected under the ORR conditions (0.7 to 0.2 V 𝑅𝐻), indicating that no emergence of structural defects could be observed during the reaction. This further precludes the possible involvement of any carbon defects in the 2e⁻ ORR process on CNB-ZIL 8. Notably, higher pyrolysis temperatures lead to the appearance of D and G bands in the Raman spectra of CNB-ZIL 9 and 10 (Figure S11a), suggesting the emergence of a slightly more crystalized graphitic carbon network with structural defects that gradually forms under high temperatures. However, despite the appearance of possible structural defects, no detectable changes on the full width at half peak maximum (FWHM) of D and D' (at ~1620 cm⁻¹) bands in Raman spectra can be observed for CNB-ZIL 9 regardless of applied potentials during ORR, indicating the lack of an interaction between carbon defects with ORR intermediates, which also rules out their possible contribution to the catalytic performance. Thus, based on the Raman measurements above, the possible interference of carbon structural defects on ORR activity can be eliminated.
Figure S12. Chronoamperometry test of CNB-ZIL 8 in O\textsubscript{2}-saturated 0.1 M KOH solution after the 12-h durability test. The CNB-ZIL loaded carbon fiber paper electrode was washed with deionized water several times before the chronoamperometry test, and the electrolyte was refreshed after the durability test. The chemical titration result gives a FE close to 87\% on CNB-ZIL 8 after the durability test, further suggesting a stable catalytic performance of the catalysts.
Figure S13. Optical photo image of flow reactor employed for electrolytic HO$_2^-$ generation. 0.1 M KOH was used as electrolyte during the whole reaction process, and the CNB-ZIL 8-loaded carbon fiber electrode and a Ni$_{1-x}$Fe$_x$OH-loaded iron foam were directly employed as the gas-diffusion cathode and the anode in the flow cell, respectively.
Figure S14. Chronoamperometry of flow reactor under a cell voltage of -1.4 V with O₂-saturated 0.1 M KOH. The signal interruptions during the bulk electrolysis in the flow cell were caused by sampling the electrolyte from the reactor. The equivalent amount of fresh electrolyte was added into the reactor once a certain amount of HO₂⁻-containing electrolyte was collected.

Supplementary Tables:

Table S1. Summarization of B, N, O and C content in the different CNB-ZIL samples based on the XPS measurements.

| Sample   | B (atom%) | C (atom%) | N (atom%) | O (atom%) |
|----------|-----------|-----------|-----------|-----------|
| CNB-ZIL 8| 21.2      | 27.0      | 24.6      | 27.2      |
| CNB-ZIL 9| 27.9      | 26.5      | 26.1      | 19.5      |
| CNB-ZIL 10| 22.4     | 35.2      | 18.3      | 24.2      |
Table S2. Summarization of the content of different BₓNᵧCₓ species in the different CNB-ZIL catalysts based on the XPS measurement. The content of B⁵ could be ascribed to the B-O bond. The ratio means the percentage of a certain BₓNᵧCₓ group in the total B content, and the atom% reflects the amount of a certain BₓNᵧCₓ group in the whole materials.

| Sample  | B1 (ratio/atom%) | B2 (ratio/atom%) | B3 (ratio/atom%) | B4 (ratio/atom%) | B5 (ratio/atom%) |
|---------|------------------|------------------|------------------|------------------|------------------|
| CNB-ZIL 8 | 11.8/2.50        | 42.3/8.97        | 41.8/8.86        | 4.1/0.87         |                  |
| CNB-ZIL 9 |                  | 17.9/4.99        | 45.0/12.56       | 29.7/8.29        | 7.4/2.06         |
| CNB-ZIL 10 |                | 15.2/3.40        | 46.9/10.51       | 29.3/6.56        | 8.6/1.93         |

Table S3. Summarization of the content of different nitrogen species in the different CNB-ZIL catalysts based on the XPS measurement. The ratio means the percentage of a certain N group in the total N content, and the atom% reflects the amount of a certain nitrogen moiety in the whole materials.

| Sample  | N1 (ratio/atom%) | N2 (ratio/atom%) | N3 (ratio/atom%) | N4 (ratio/atom%) | N5 (ratio/atom%) |
|---------|------------------|------------------|------------------|------------------|------------------|
| CNB-ZIL 8 | 34.7/8.54        | 33.3/8.19        |                  |                  | 32.0/7.87        |
| CNB-ZIL 9 | 17.9/4.67        | 45.0/11.75       | 29.7/7.75        | 7.4/1.93         |                  |
| CNB-ZIL 10 | 15.2/2.78        | 46.9/8.58        | 29.3/5.36        | 8.6/1.57         |                  |
Table S4. Comparisons of the electrocatalytic activities of noble-metal-free 2e⁻ ORR catalysts. $E_{\text{onset, ORR}}$ represents the required operation potential to initiate the ORR process. (Operation conditions: 0.1 M KOH)

| Catalyst          | $E_{\text{onset, ORR}}$ (V RHE) | Selectivity at different potentials (% @ V_RHE) | Productivity | Reference |
|-------------------|--------------------------------|-----------------------------------------------|--------------|-----------|
| BN-C1             | 0.80 @ 0.5 mA cm⁻²             | ~78% @ 0.4 V_RHE                             | N/A          | [4]       |
| MesoC             | 0.7                            | ~70% @ 0.3 V_RHE                             | N/A          | [5]       |
| CMK-3             | ~0.8 for ring current          | ~85% @ 0.3 V_RHE                             | 1397.5 mg L⁻¹ h⁻¹ | [6]       |
| AQ-C₃N₄          | 0.5                            | 42.2% @ -0.22 V_RHE                          | 60.1 mmol g⁻¹ h⁻¹ | [7]       |
| NiN₆/C-AQNH₂      | ~0.76@ 0.5 mA cm⁻²             | ~81% @ 0.6 V_RHE                             | N/A          | [8]       |
| O-CNTs            | ~0.75@0.25 mA cm⁻²             | ~87% @ 0.4 V_RHE                             | ~111.7 mmol g⁻¹ h⁻¹ | [9]       |
| CB+CTAB          | ~0.75@0.2 mA cm⁻²              | ~90% @ -0.1 V_RHE                            | N/A          | [10]      |
| B-C               | ~0.8                           | ~84% @ 0.4 V_RHE                             | 7.36 mmol cm⁻² h⁻¹ | [11]      |
| Mo₁/OSG-H        | ~0.82                          | ~93% @ 0.3 V_RHE                             | N/A          | [12]      |
| OCNS₉₀₀          | ~0.85                          | ~90% @ 0.5 V_RHE                             | 770 mmol g⁻¹ h⁻¹ | [13]      |
| o-GOMC-1         | ~0.8                           | ~85% @ 0.2 V_RHE                             | N/A          | [14]      |
| Co₁-NG(O)        | ~0.8                           | ~78% @ 0.5 V_RHE                             | 418 ±19 mmol g⁻¹ h⁻¹ | [15]      |
| OMPC4            | ~0.7                           | ~80% @ 0.4 V_RHE                             | N/A          | [16]      |
| MCHS-9:1         | ~0.81                          | ~55% @ 0.4 V_RHE                             | N/A          | [17]      |
| (I-C₆₀)@SWNT     | ~0.75                          | ~78% @ 0.4 V_RHE                             | N/A          | [18]      |
| g-N-CNHs         | ~0.75                          | ~20% @ 0.5 V_RHE                             | 73 mmol g⁻¹ h⁻¹ cm⁻² | [19]      |
| NF-Cs         | ~0.75 for ring current | ~79% @ 0.52 $V_{\text{RHE}}$ | N/A      | [20]  |
|--------------|-------------------------|-------------------------------|----------|------|
| CNB-ZIL 8    | ~0.8 @ 0.1 mA cm$^{-2}$ | ~87% @ 0.3 $V_{\text{RHE}}$ (bulk electrolysis) | ~1787 mmol$^{-1}$ h$^{-1}$ | This work |

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