

## Tunable nitrogen-doped carbon aerogels as sustainable electrocatalysts in the oxygen reduction reaction – Electronic Supplementary information (ESI)

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### Experimental

D-(+)-glucose was purchased from Roth chemicals. Borax (SIGMA grade) and 2-pyrrol-carboxaldehyde (PCA) were purchased from Sigma Aldrich. All chemicals were used as received.

For each experiment, 6.0 g Glucose were dissolved in 14.0 g distilled water. X g PCA and Y g Borax then added to the solution whereby X = 0.8 g (label N1), 1.3 g (label N2) or 2.0 g (label N3) and Y = 150 mg (label B1), 300 mg (label B2) or 600 mg (label B3). To obtain an undoped carbon aerogel, 300 mg Borax were added to the glucose solution while no PCA was added. The solution was filled into a glass inlet which was then placed in a Teflon lined, stainless steel autoclave (45 ml volume, purchased from Parr Instruments). The autoclave was placed in a pre-heated furnace at 180 °C for 18 h after which it was allowed to cool down to room temperature. The resulting hydrothermal monoliths were washed with excess water and ethanol to remove Borax and any organic residues. Finally supercritical CO<sub>2</sub> drying was carried out to yield a low density carbonaceous aerogel.

For pyrolysis, the dried sample was placed in a ceramic crucible and covered with a ceramic lid. The crucible was placed in a nitrogen atmosphere furnace and flushed for 30 minutes before heating to 900 °C at a heating rate of 10 K min<sup>-1</sup>. The final temperature was kept for 4 h after which the furnace was allowed to cool down to room temperature. The obtained black monoliths were ground to fine powders prior to further characterization. The suffix **\_900** was added to the corresponding sample labels.

## Physical and Chemical Sample Characterization

**N<sub>2</sub> sorption analysis** was performed at 77 K using a QUADROSORB SI, equipped with automated surface area and pore size analyzer. Before analysis, samples were degassed at 60 °C (organic aerogels) or 150 °C (carbon aerogels) for 20 h using a “Masterprep” degassing system. Quenched Solid Density Functional Theory (QSDFT) pore size distributions (PSD) were calculated using, as this evaluation model takes into account the effects of surface roughness and chemical heterogeneity of the material surfaces. Material morphology was visualized using a Gemini Scanning Electron Microscope (**SEM**). Transmission Electron Microscopy (**TEM**) was carried out with a Carl Zeiss Omega 912X at an acceleration voltage of 120 kV. Samples for High resolution transmission electron microscopy (**HRTEM**) were prepared by dry deposition of the material onto holey carbon copper grids. **HRTEM** was performed using a Philips CM 200 microscope with a field emission gun operated at 200kV. **XRD** patterns were recorded on a Bruker D8 diffractometer over the 2θ range of 5 to 80° using Cuα radiation and a scan rate of 1 ° min<sup>-1</sup>.

**Elemental analysis** of C, H, N and S was obtained on a Vario El elemental analyzer. **XPS analysis** of the samples was performed using a Thermo Scientific Kα ESCA instrument equipped with Al Kα<sub>1, 2</sub> monochromatized radiation at 1486.6 eV X-ray source. Charge neutralization was performed by using both a low energy flood gun (0 to 14 eV) and a low energy Ar ion gun. The XPS measurements were carried out using monochromatic Al-Kα radiation (hν = 1486.6 eV). Photoelectrons were collected at 90° to the sample surface. A constant analyzer energy mode (CAE) with 100 eV pass energy for survey spectra and 20 eV pass energy for high resolution spectra was used. The spectra were calibrated by setting the C1s photo peak at 285.0 eV. Surface elemental composition was determined using standard Schofield photoemission cross sections. Peak assignments were carried out by using the values reported in the NIST XPS Database iii and references indicated in the text. . **Specific conductivity measurements** were carried out with Gamry Reference 600/3000 potentiostat

(Gamry Instruments) and Gamry EIS 300/Physical Electrochemistry software. Electrical conductivity was achieved applying R-model on potentiostatic impedance spectroscopy at 1-1000 Hz using a two electrode setup. To perform **electrochemical testing** a standard ink was prepared from ~5 mg of catalyst (ground monolith powder) with 95  $\mu\text{l}$  Nafion® binder solution and 350  $\mu\text{l}$  of ethanol. The ink was ultrasonicated for at least 30 minutes for homogenization. A 5  $\mu\text{l}$  aliquot was dropped onto a freshly polished glassy carbon rotating disk electrode (diameter ~ 5 mm, electrode area 0.196  $\text{cm}^2$ ) to prepare a catalyst thin film. When necessary, the electrode was warmed to ~ 50 °C in an oven prior to ink application in order to achieve better electrode coverage of the catalyst film. Electrochemical tests were performed in 0.1 M KOH in a standard three - electrode setup with an Ag / AgCl reference electrode and a platinum counter electrode using Gamry Reference 600 potentiostat (Gamry Instruments) and Gamry EIS 300/Physical Electrochemistry software. Cyclic voltammetry was carried out at a scan rate of 100  $\text{mV s}^{-1}$  while all other measurements were carried out using a scan rate of 10  $\text{mV s}^{-1}$ . The obtained current values were normalized to the mass of the catalyst used (*i.e.* given in  $\text{mA mg}^{-1}$ ) for direct comparison between samples. For **Koutecky-Levich analysis**, the un-normalized currents obtained from measurements at varying rotation rates (600, 1000, 1600, 2000, and 2600 rpm) were used.

The Levich current,  $I_{lev}$ , is given by

$$I_{lev} = 0.62nFAD^{\frac{2}{3}}\omega^{\frac{1}{2}}\nu^{-\frac{1}{6}}C$$

where

- n number of electrons transferred in the half reaction
- F Faraday constant
- A electrode area
- D diffusion coefficient of the reactant in the electrolyte
- $\omega$  angular rotation rate of the electrode
- $\nu$  kinematic viscosity of the electrolyte
- C analyte concentration

The kinetic current,  $I_k$  is given by:

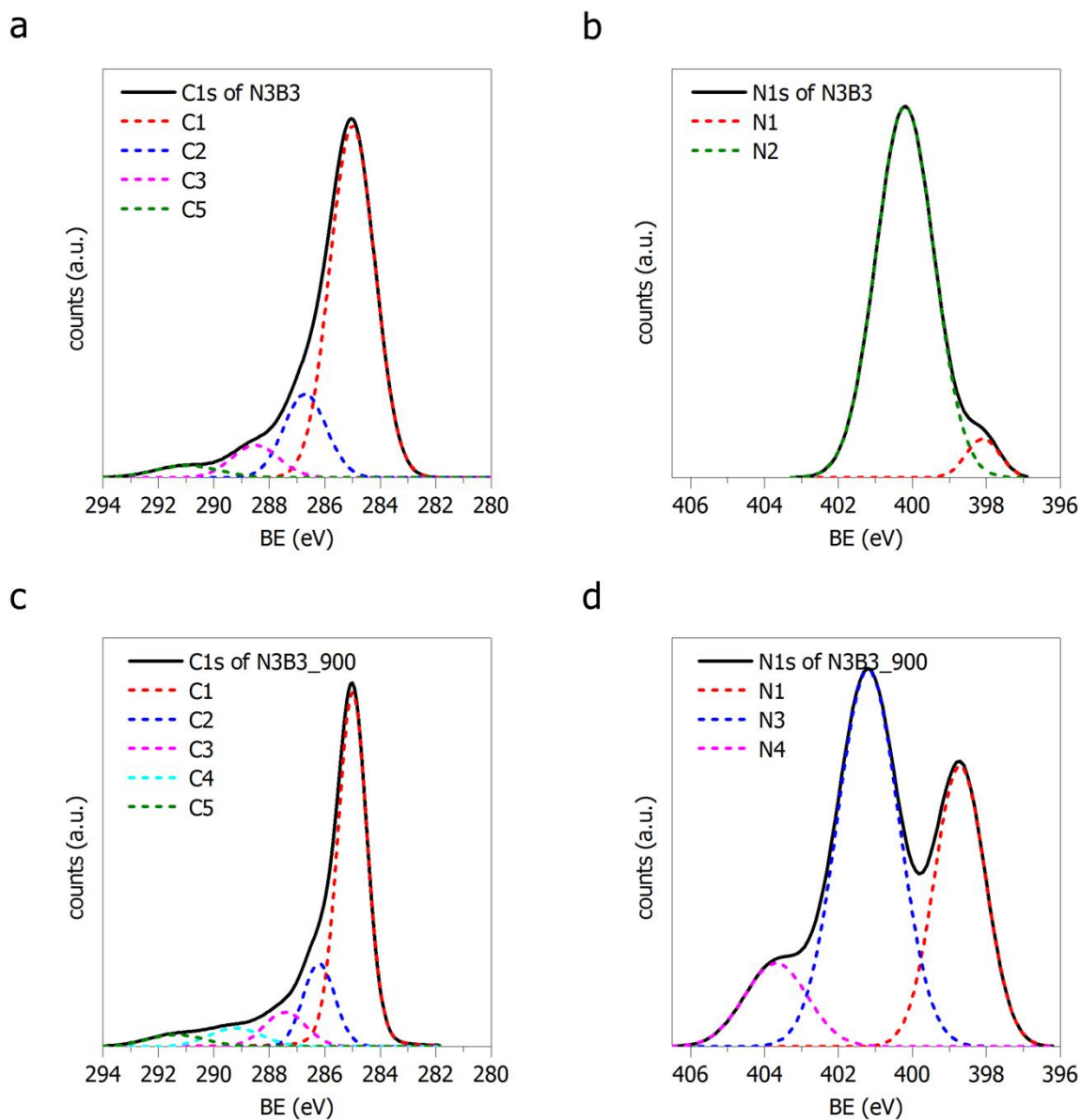
$$I_k = nFAkC\Gamma_{cat}$$

- n number of electrons transferred in the half reaction  
F Faraday constant  
A electrode area  
k pseudo second order rate constant  
C analyte concentration  
 $\Gamma_{cat}$  catalyst loading

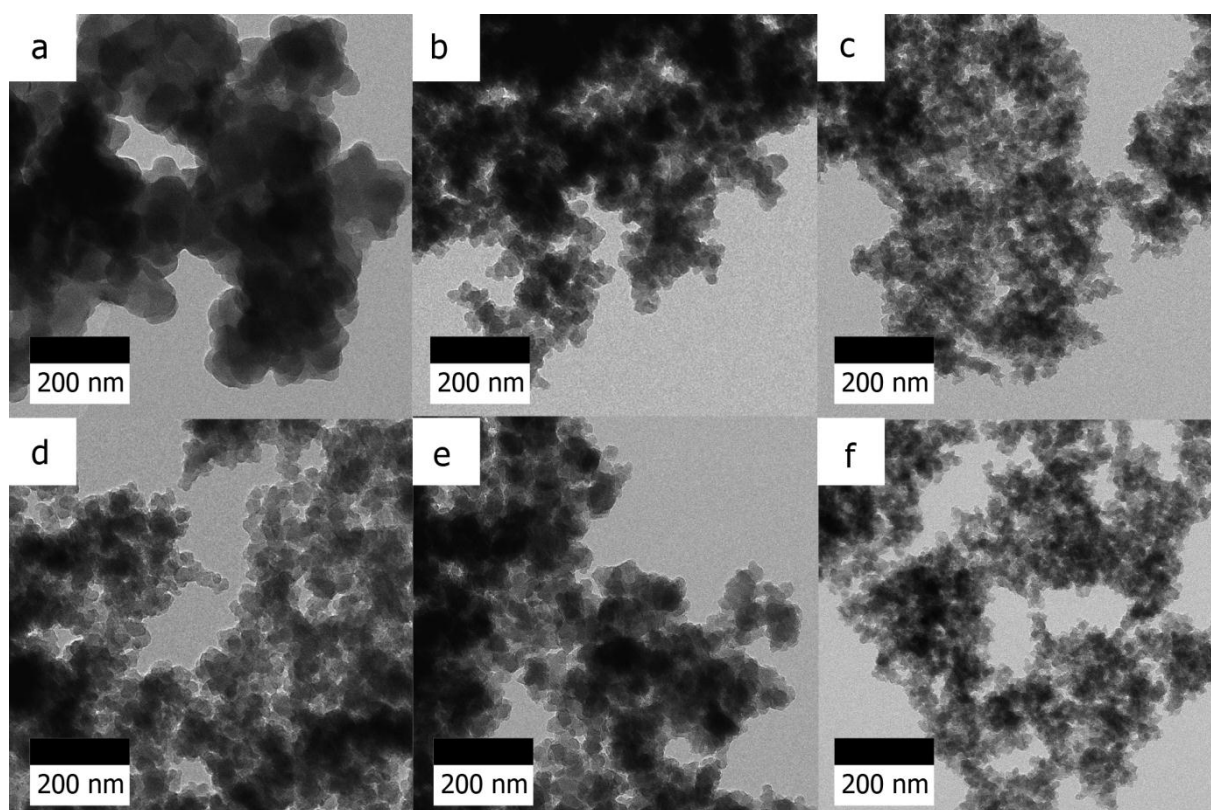
Combining both equations leads to the Koutecky-Levich expression, which describes the overall RDE current  $I$  for the electrocatalytic reaction over the entire potential range:

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{I_{lev}}$$

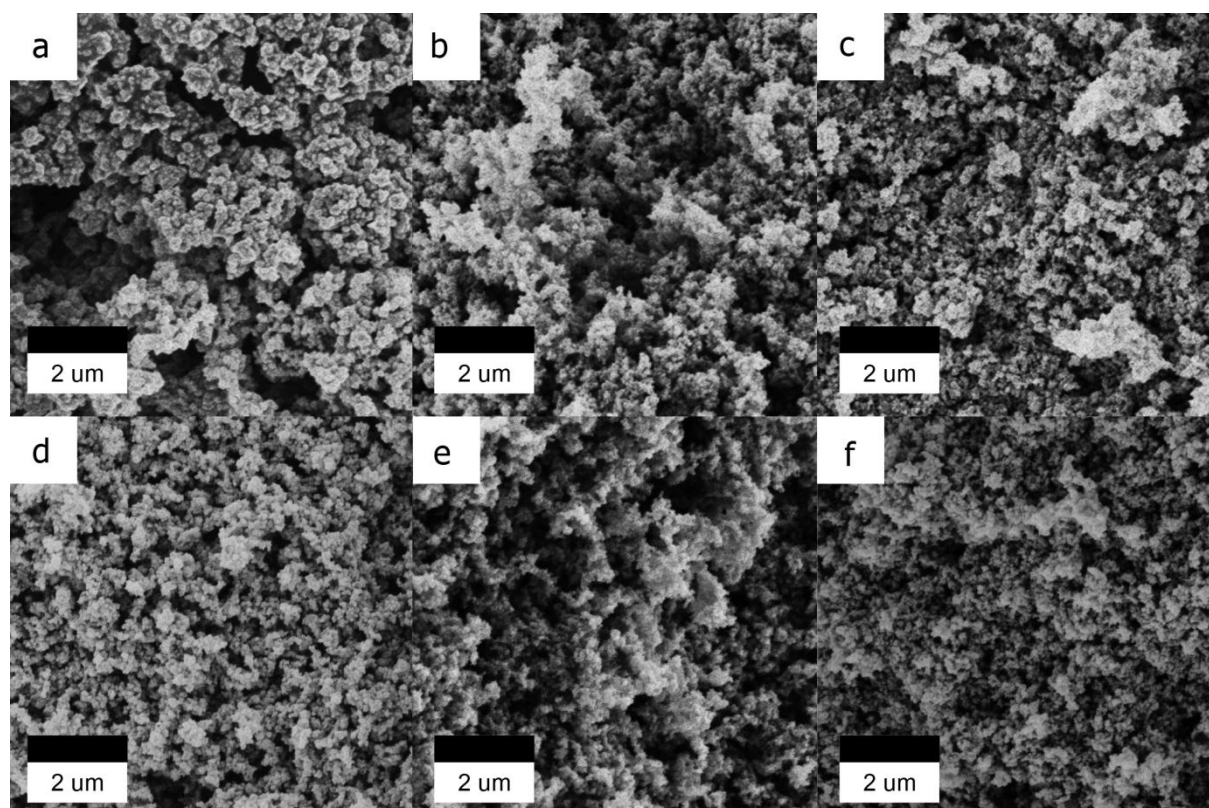
A plot of  $\frac{1}{I}$  against  $\frac{1}{\omega^{1/2}}$  should yield a straight line whose slope is related to the **number of electrons** transferred in the reaction, and whose intercept is related to the kinetic current.



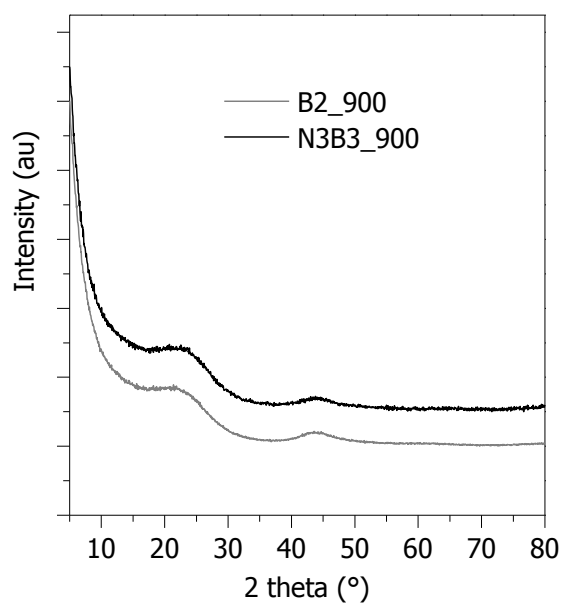
**Figure S 1 Deconvoluted C1(s) and N1(s) photoelectron envelopes of N3B3 (a and b, respectively), and N3B3\_900 (c and e, respectively)**



**Figure S 2 TEM images of a) N1B1\_900, b) N1B2\_900, c) N1B3\_900, d) N2B2\_900, e) N3B2\_900 and f) N3B3\_900**



**Figure S 3 SEM images of a) N1B1\_900, b) N1B2\_900, c) N1B3\_900, d) N2B2\_900, e) N3B2\_900 and f) N3B3\_900**



**Figure S 4 XRD diffractograms of undoped carbon aerogel and a representative**

## nitrogen doped carbon aerogel

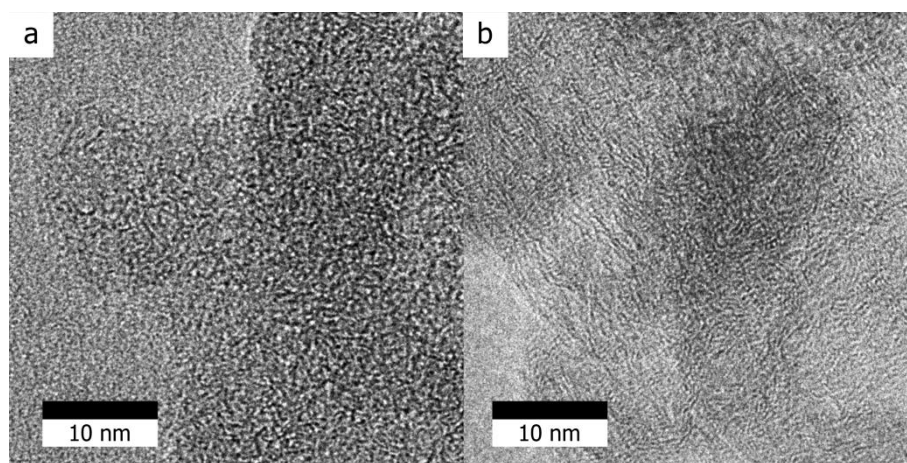


Figure S 5 HRTEM images of (a) B2\_900 and (b) N3B3\_900

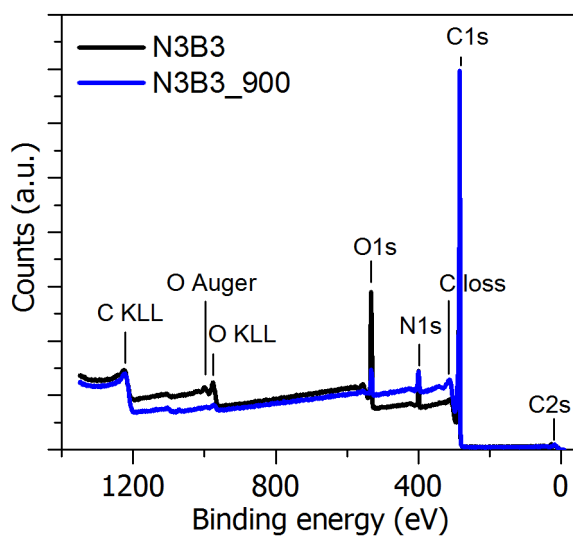


Figure S 6 XPS survey scans of N3B3 and N3B3\_900