A Sustainable Synthesis of Nitrogen-Doped Carbon Aerogels

Supporting Information

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Characterisation Details:

N_2 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 150 °C for 20 h using a "*Masterprep*" degassing system. BET surface areas were determined over a P/P_0 range as described previously.[i] 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 these functional nitrogen-doped *Carbogel* surfaces (Figure 2S).[ii] "*Carbogel*" density was determined via Hg intrusion porosimetry, using a Porotec GmbH Pascal analyzer. Prior to analysis the sample was heated in an oven at 120 °C for 24 h. An initial measurement was made using a Pascal 140 using low pressure (400 kPa) followed by secondary analysis using a Pascal 440 at high pressure (400 MPa). 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. High Resolution (HR) TEM images were acquired using a TOPCON EM-002B at an operating voltage of 120 kV. Prior to analysis samples lightly ground in a mortar, and then suspended in distilled water using ultrasonic treatment. Approximately 5 µL of the suspension was then dropped onto a Cu microgrid mesh. TEM observation was carried using the prepared grid after evaporative drying. Elemental analysis was obtained on a Vario El elemental analyzer. XPS analysis was performed using a Thermo Scientific K-Alpha ESCA instrument equipped with Al Kα monochromatized radiation at 1486.6 eV X-ray source. Surface charge neutralization was performed by using both a low energy flood gun (electrons in the range 0 to 14 eV) and a low energy Argon ion gun. Photoelectrons were collected using a take off angle of 90 º relative to the sample surface, in a Constant Analyzer Energy mode with 100 eV pass energy for survey spectra and 20 eV pass energy for high resolution spectra. Charge referencing was done by setting the lower binding energy C 1s photo peak at 285.0 eV C 1(s) hydrocarbon peak. 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. Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) surface mapping was performed using a TOF-SIMS IV instrument (Ion-ToF GmbH, Germany). The sample was bombarded with a pulsed Bismuth ion beam and the 2^o ions generated extracted with a 10 KV voltage and their time of flight from the sample to the detector was measured in a Reflectron mass spectrometer. Typical analysis conditions involved a pulsed 25 keV Bi_3 beam at 45 º incidence, rastered over an area of 500 x 500 μm^2. Electron flood gun for charge compensation was used during measurements.

Supplementary Results.

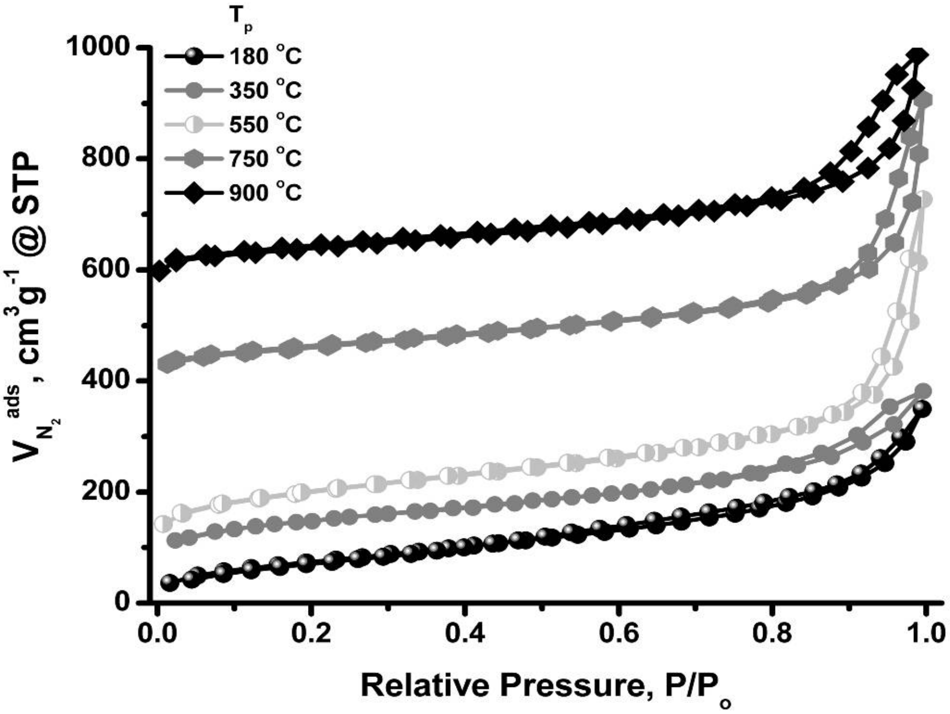

Figure 1S. N_2 sorption isotherms of hydrothermal "*Carbogel*" and materials-derived there from prepared at increasing T_p (i.e. 350 - 900 °C). *[NB: Isotherms are offset relative to 180 °C sample by 85 cm^{3}g^{-1} (@ 350 °C), 60 cm^{3}g^{-1} (@ 550 °C), 380 cm^{3}g^{-1} (@ 750 °C) and 550 cm^{3}g^{-1} (@ 900 °C) respectively].*

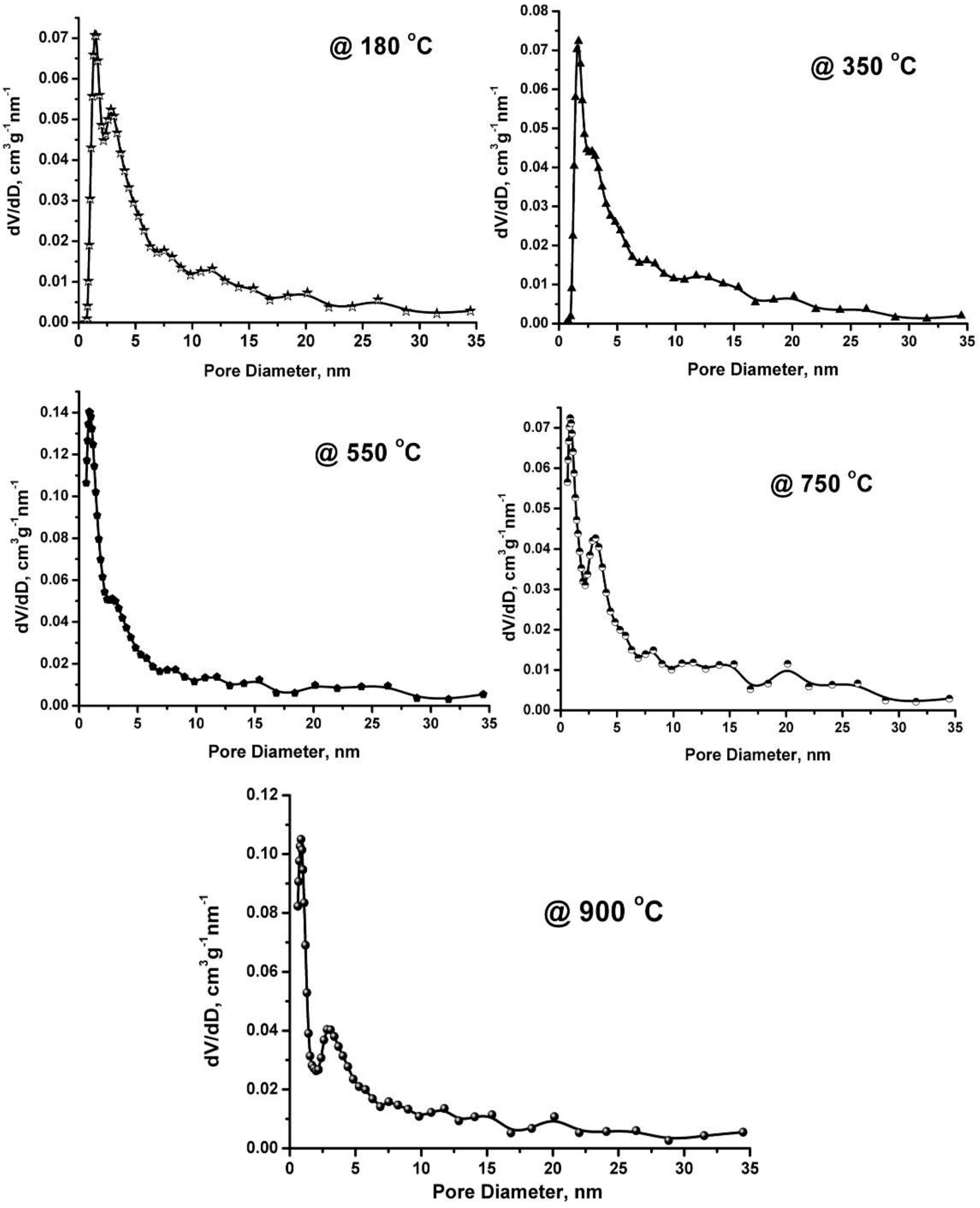

Figure 2S. QSDFT Pore size distributions for "*Carbogels*" and post-carbonized derivatives.

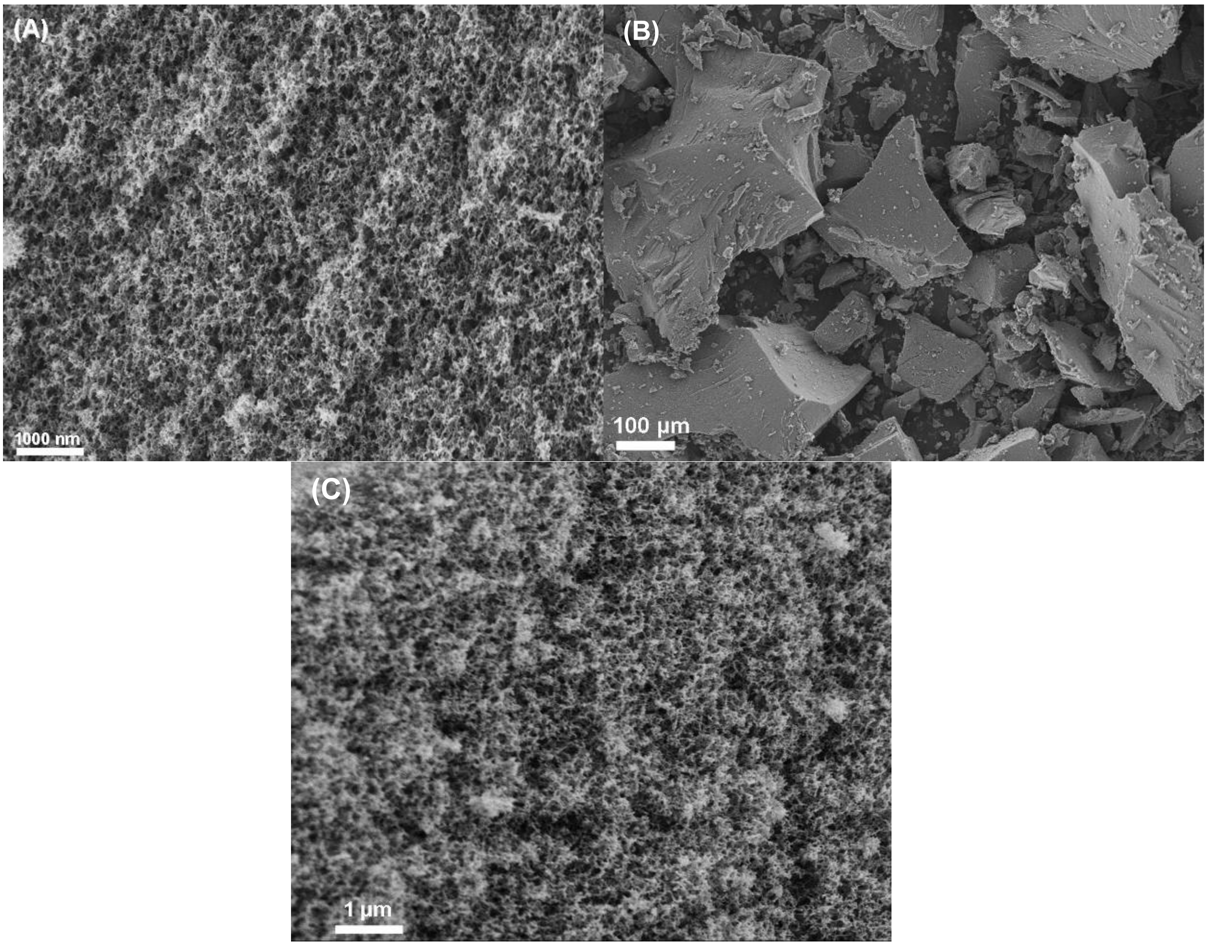

Figure 3S. Representative SEM images of *Carbogels* after further carbonization at (A) 350 ^{o}C, (B) (cracked monolith)) 550 ^{o}C and (C) 900 ^{o}C.

Please see additional video file.

Figure 4S. 3D HR TEM topography video of “Carbogel” prepared at 900 ^{o}C

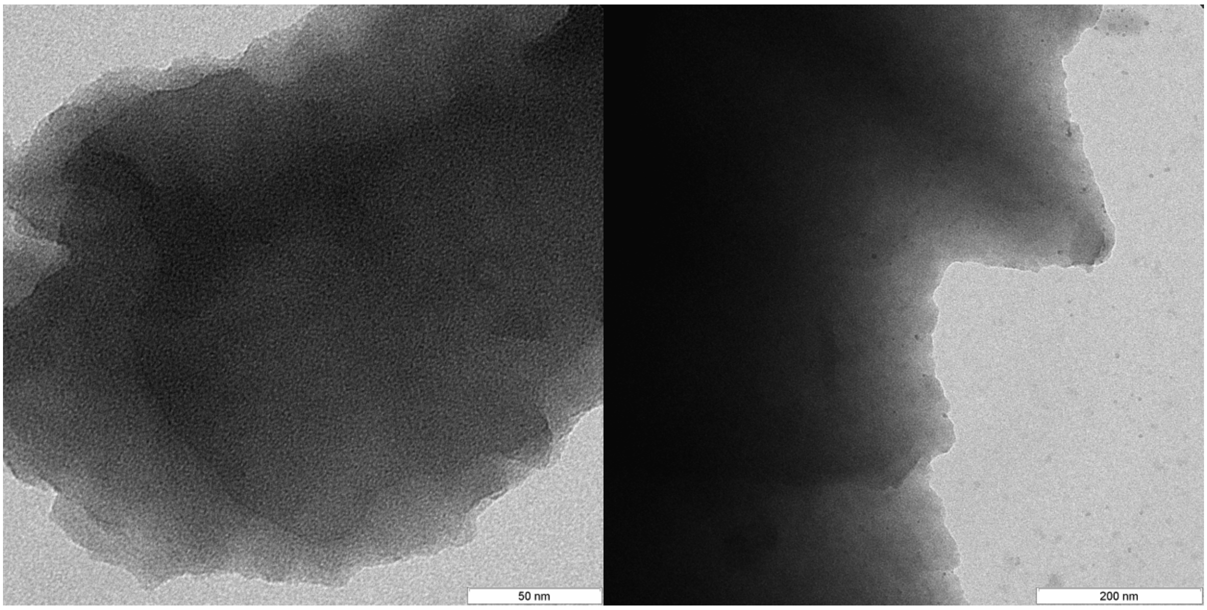

Figure 5S. TEM images of materials heated to 550 °C prepared from "*Carbogel*" precursors synthesized after **(A)** 2 h and **(B)** 4 h HTC heating time.

Further XPS Analysis Details:

Table 1S. Changes in Chemical bonding of Carbon 1(s) photoelectron envelope as a function of carbonisation temperature (T_p).

	Binding energy (B.E., eV) / Relative %			
T_p, °C	**C1** **[-CH_x / C-C]** **(284.6 – 285.0)**	**C2** **[-C-N / C=N]** **(285.9-286.4)**	**C3** **[-C=O / C=O-N]** **(287.7-288.4)**	**C4 (290.37)** **[$\pi \rightarrow \pi^*$]** *“shake up”*
180	285.0 / 48.1	286.27 / 35.9	288.33 / 15.9	-
350	285.0 / 63.6	286.33 / 22.1	288.05 / 14.3	-
550	285.0 / 77.6	286.14 / 18.5	287.88 / 3.9	-
750	285.0 / 74.9	286.14 / 23.1	288.02 / 2.0	-
900	285.0 / 68.4	286.28 / 15.9	287.77 / 9.1	290.37 / 6.6

Table 2S. Changes in chemical bonding of the N 1(s) photoelectron envelope as a function of carbonisation temperature (T_p).

	Binding energy (B.E., eV) / Relative %				
^aT_p, °C	**N1** **[“Amine”]** **(399.2-399.5)**	**N2** **[“Pyridine”]** **(398.5-398.8)**	**N3** **[“Pyrrole”]** **(400.2-400.4)**	**N4** **[“Quartenary”]** **(401.0-401.5)**	**N5** **[“Pyr-N-Oxide”]** **(403.4-403.9)**
180	399.46 / 24.3	-	400.29 / 65.0	401.50 / 10.7	-
350	399.24 / 32.7	-	400.37 / 51.0	401.44 / 16.3	-
550	-	398.78 / 43.6	400.28 / 40.9	401.01 / 15.4	-
750	-	398.65 / 37.5	-	401.22 / 46.0	403.85 / 16.5
900	-	398.53 / 38.7	-	401.15 / 45.2	403.35 / 16.2

[a] Preparation temperature

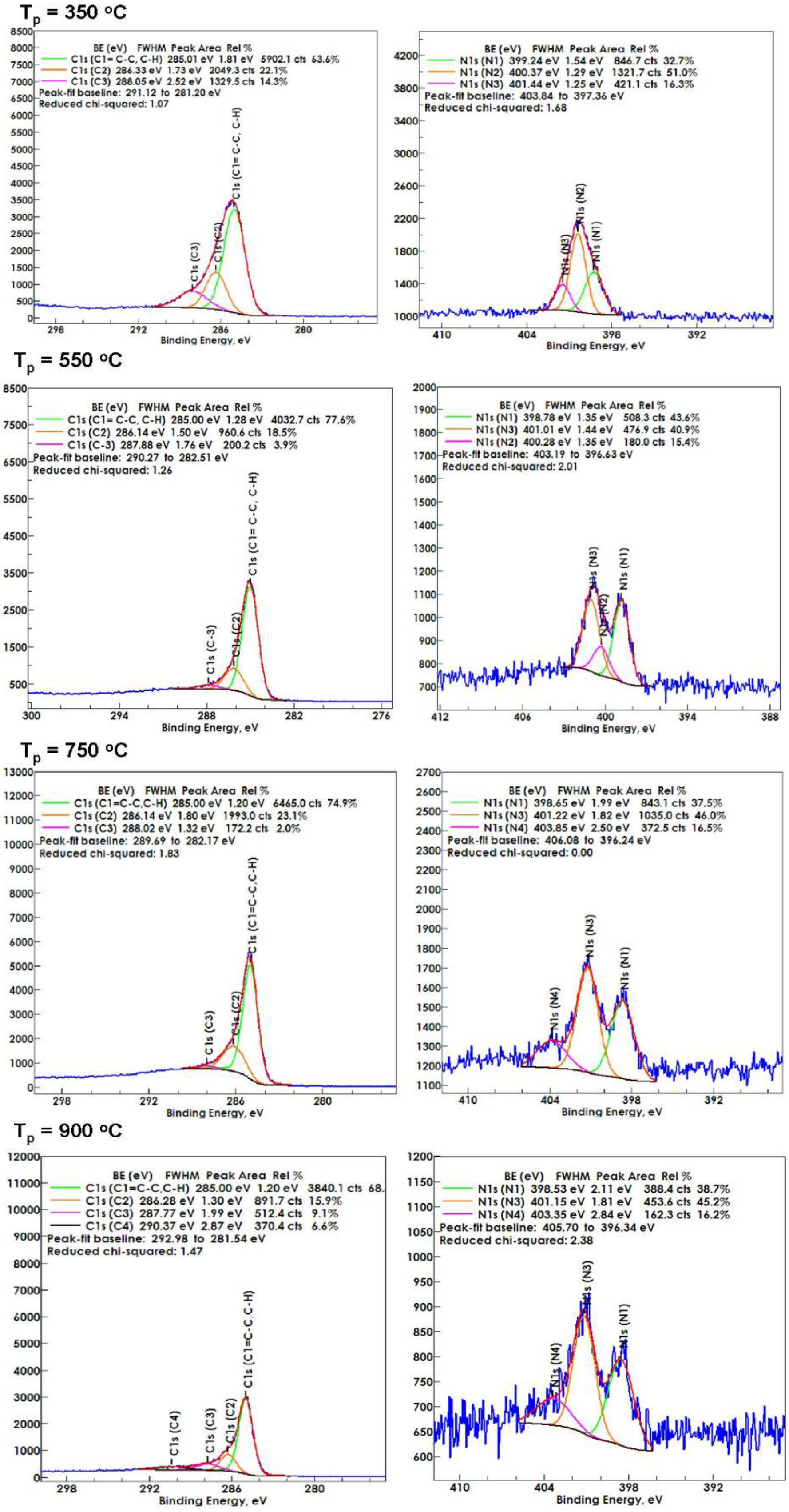

Figure 7S. High resolution XPS scans of the C 1(s) and N 1(s) photoelectron envelopes for "*Carbogels*" prepared at increasing T_p.

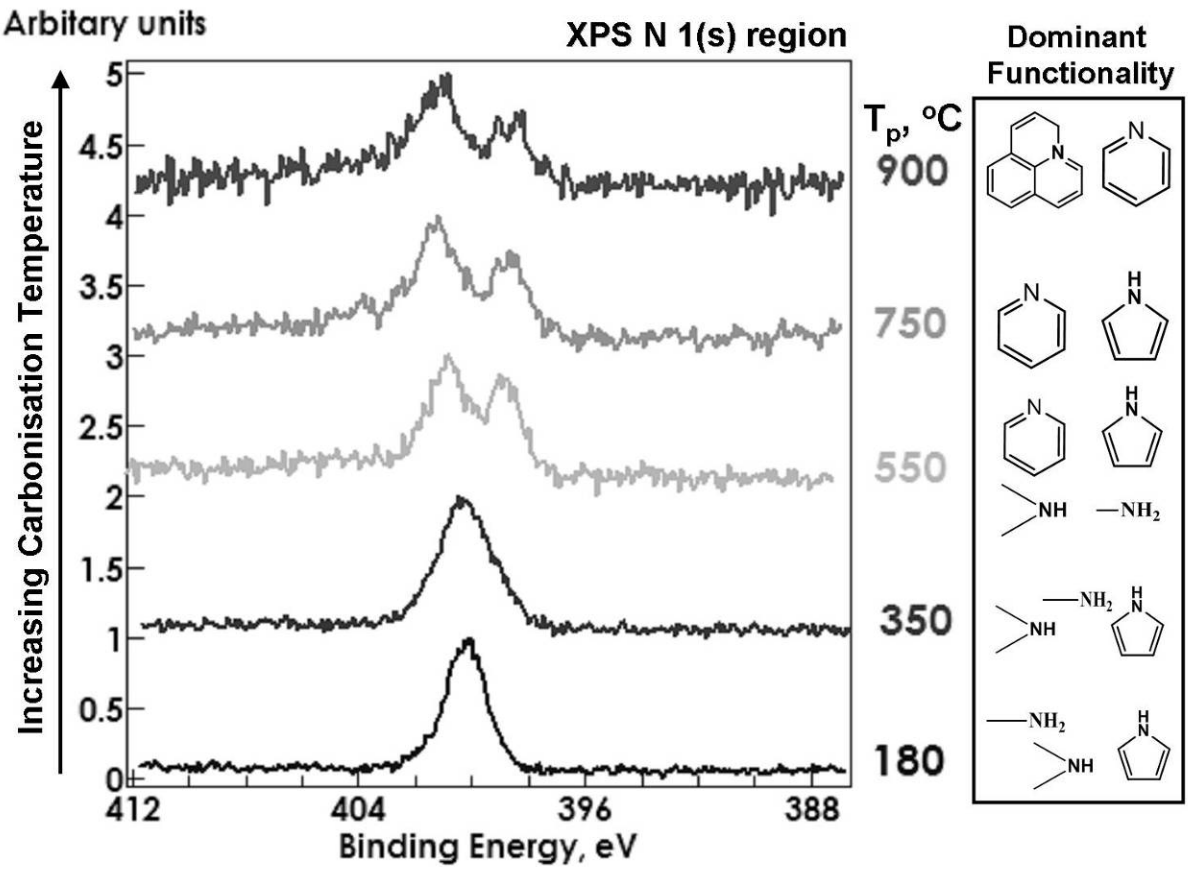

Figure 8S. Normalised high resolution XPS of the N 1(s) photoelectron envelope displayed as a function of carbonisation temperature (T_p).

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[i] K. S. Walton, R. Q. Snurr, *J. Am. Chem. Soc.* 2007, **129**, 8552

[ii] P. I. Ravikovitch, A. V. Neimark, Langmuir 2006, **22**, 26, 11171.

[iii] X-ray Photoelectron Spectroscopy Database 20, Version 3.0, National Institute of Standards and Technology, Gaithersburg, MD; http://srdata.nist.gov/XPS