Carbon-based ionogels: tuning the properties of the ionic liquid via carbon-ionic liquid interaction

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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 ^{o}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]

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.

Supplementary Information

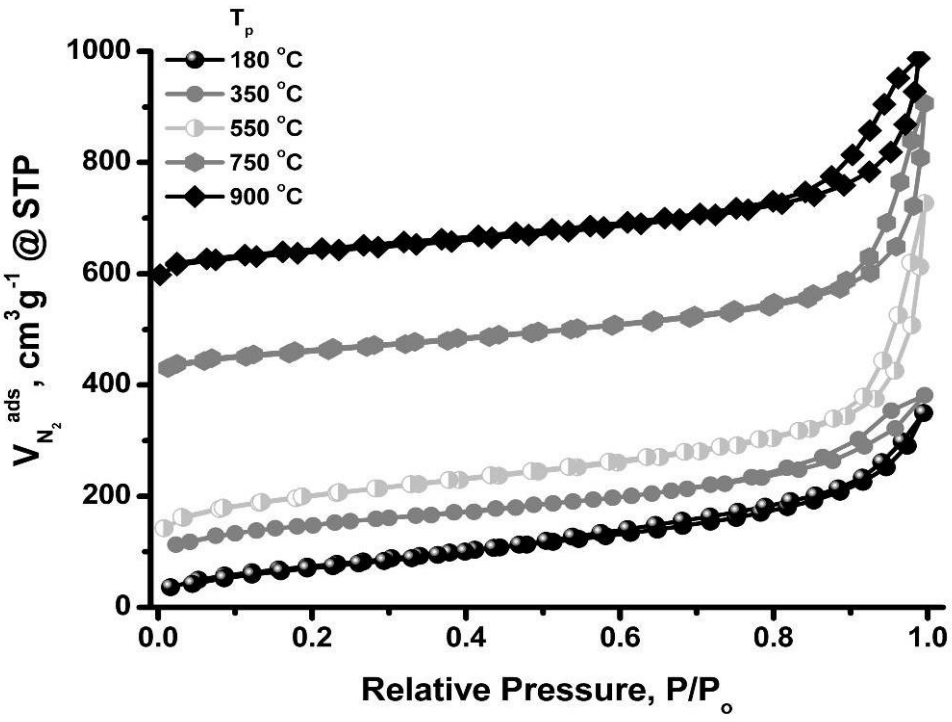


Figure S1. N_2 sorption isotherms of hydrothermal "*Carbogel*" and materials-derived there from prepared at increasing T_p (i.e. 350 - 900 ^oC). *[NB: Isotherms are offset relative to 180 ^oC sample by 85 cm^3g^{-1} (@ 350 ^oC), 60 cm^3g^{-1} (@ 550 ^oC), 380 cm^3g^{-1} (@ 750 ^oC) and 550 cm^3g^{-1} (@ 900 ^oC) respectively].*

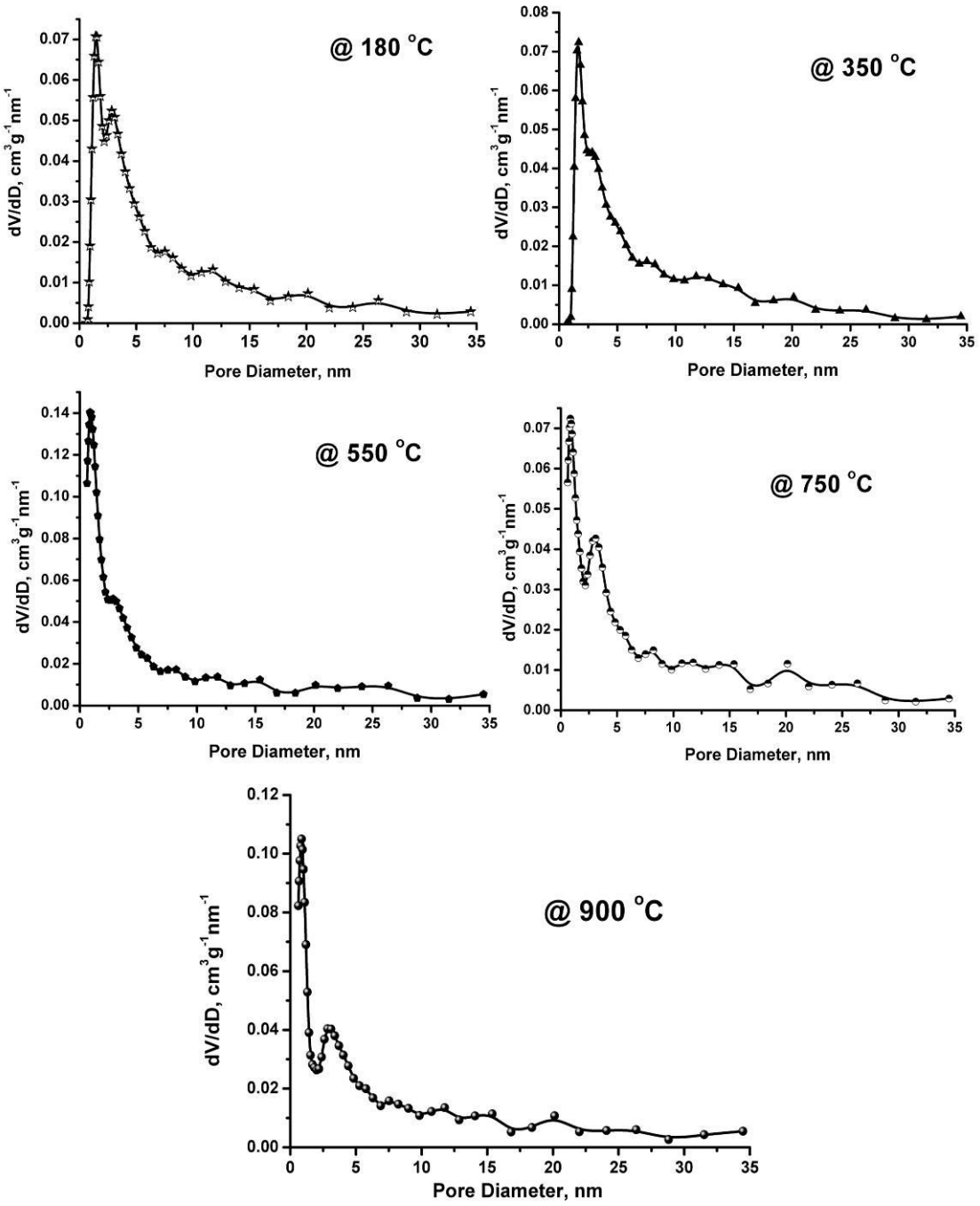


Figure S2. QSDFT Pore size distributions for "*Carbogels*" and post-carbonized derivatives.

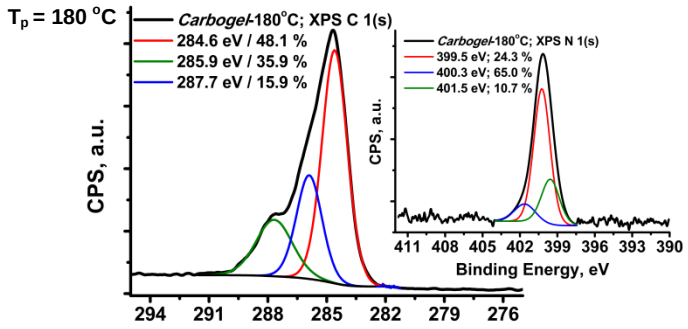
Table S1. Changes in Chemical bonding of Carbon 1(s) photoelectron envelope as a function of carbonisation temperature (T_p).

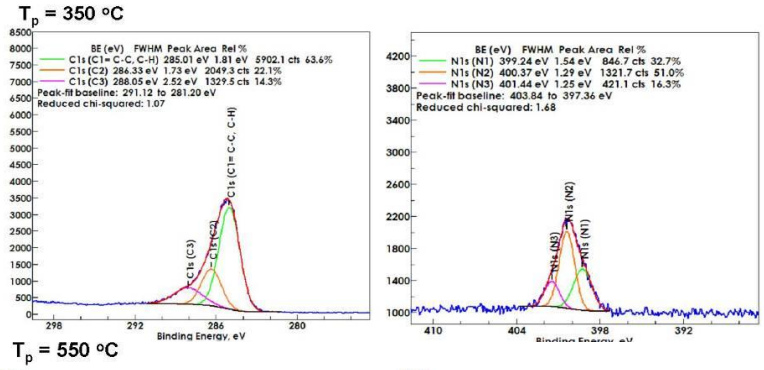
	Binding energy (B.E., eV) / Relative %			
T_p, ^{o}C	**C1 [-CH_x / C-C] (284.6 – 285.0)**	**C2 [-C-N / C=N] (285.9-286.4)**	**C3 [-C=O / C=O-N] (287.7-288.4)**	**C4 (290.37) [$\pi \rightarrow \pi^*$] *"shake-up"***
180	285.0 / 48.1	286.27 / 35.9	288.33 / 15.9	-
350	285.0 / 63.6	286.33 / 22.1	288.05 / 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

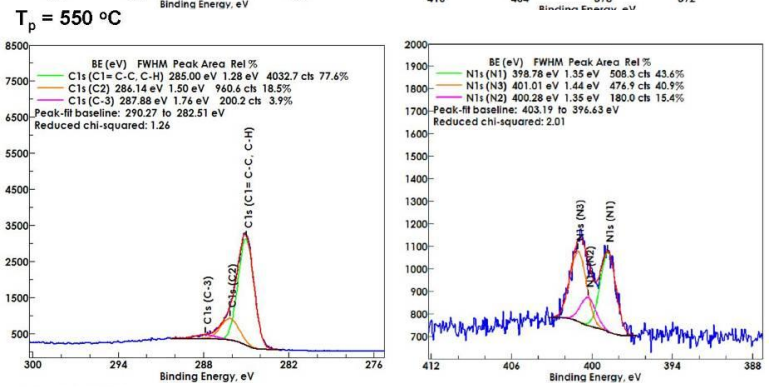
Table S2. Changes in chemical bonding of the N 1(s) photoelectron envelope as a function of carbonisation temperature (T_p).

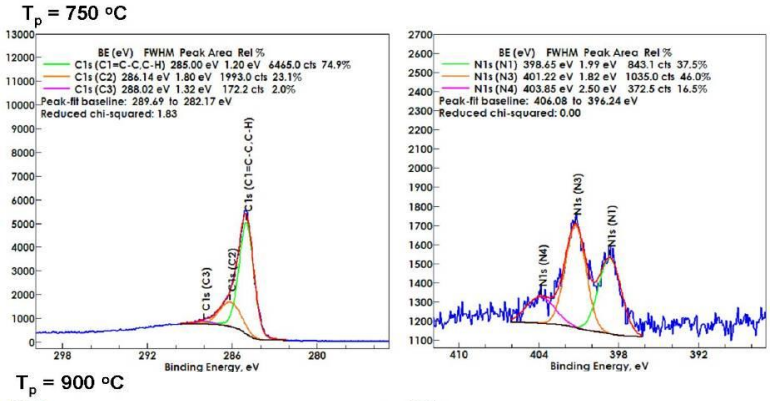
	Binding energy (B.E., eV) / Relative %				
[a] T_p, ^{o}C	**N1 ["Amine"] (399.2-399.5)**	**N2 ["Pyridine"] (398.5-398.8)**	**N3 ["Pyrrole"] (400.2-400.4)**	**N4 ["Quaternary"] (401.0-401.5)**	**N5 ["Pyr-N-Oxide"] (403.4-403.9)**
180	399.46 / 24.3	-	400.29 / 65.0	401.50 / 10.7	-
350	399.24 / 32.7	-	400.37 / 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









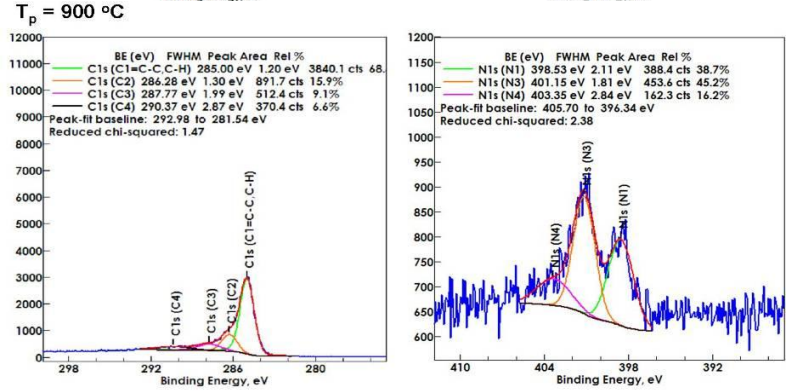


Figure S3. High resolution XPS scans of the C 1(s) and N 1(s) photoelectron envelopes for "*Carbogels*" prepared at increasing T_p.

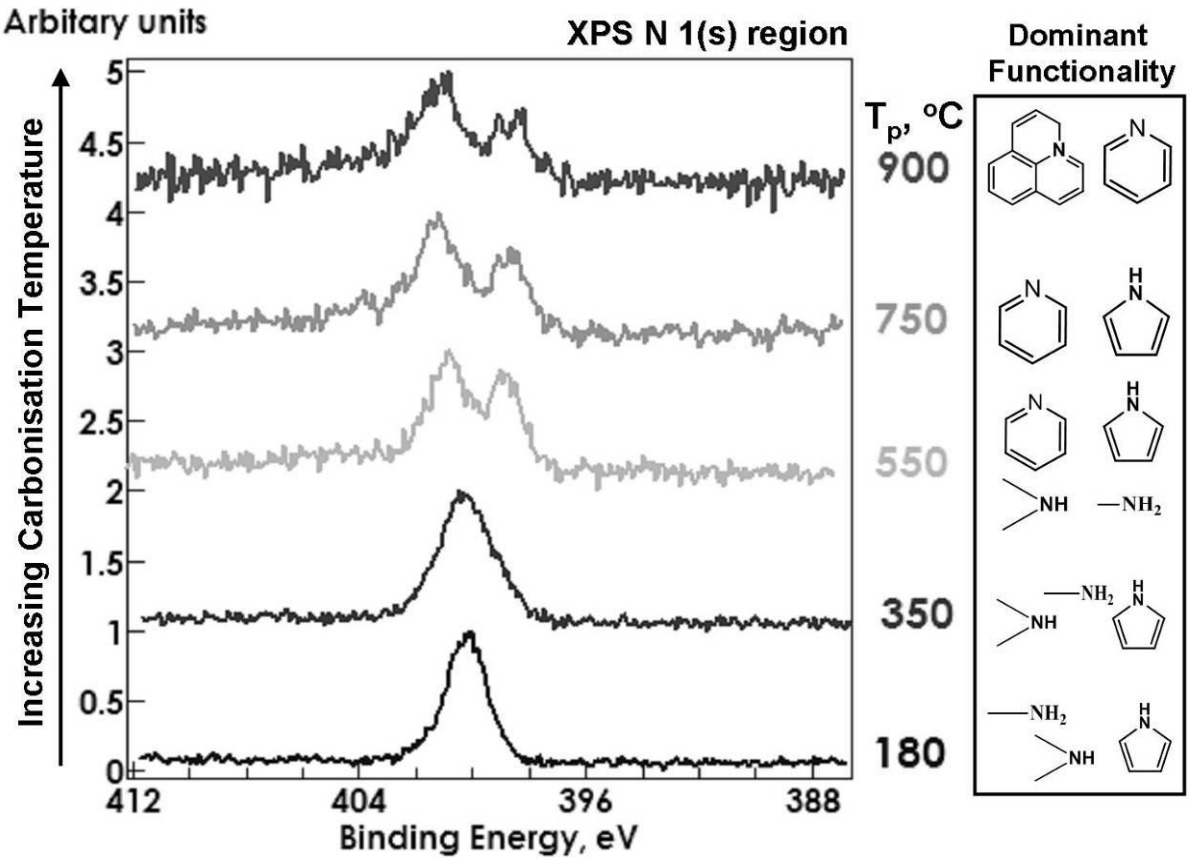


Figure S4. Normalised high resolution XPS of the N 1(s) photoelectron envelope displayed as a function of carbonisation temperature (T_p).

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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