The effect of nitrogen on the synthesis of porous carbons by iron-catalyzed graphitization

Supplementary Information

Experimental methods and materials

Materials

D-glycine (≥98.5 %), gelatin (from porcine skin – G2500), N-acetylglucosamine, chitosan (from shrimp shells - 50494), chitin (from shrimp shells – C7170), iron (III) nitrate nonahydrate, acetic acid.

Catalytic graphitization

For glycine and N-acetylglucosamine samples, 25 ml deionized water was gently heated in a beaker and 5 g of glycine was added with magnetic stirring until the glycine had completely dissolved. 0.27 g (0.67 mmol) of $Fe(NO_3)_3.9H_2O$ was dissolved in 4 ml of DI water and this was added to the glycine solution, followed by stirring for 10 min. The mixture was dried in an air oven at 70 °C for 24 hr or until constant mass. The resulting brown, caramel-like material was placed in an alumina boat crucible and heated in a tube furnace at a rate of 5 °C min^{-1} under a nitrogen atmosphere with a flow rate of 1 L min^{-1} to 800 °C. The samples were held at 800 °C for 1 h, unless otherwise stated, before cooling completely to room temperature.

For gelatin samples, the same procedure was followed except 5 g of gelatin was added to 50 ml DI water and heating to 70 °C was required to achieve dissolution before addition of $Fe(NO_3)_3$ solution. For chitosan samples, 5 g of chitosan was dissolved in 250 ml, 2 wt% acetic acid solution and stirred for 3 hr before addition of $Fe(NO_3)_3$ solution.

For chitin samples, 0.27 g (0.67 mmol) of $Fe(NO_3)_3.9H_2O$ was dissolved in 20 ml of DI water at room temperature and the resulting solution added to a beaker containing 5 g of chitin. The mixture was manually stirred until the solution had been absorbed. The sample was dried and pyrolyzed as above. Control samples from each organic precursor were prepared using the same method but without the addition of iron nitrate solution.

Powder X-ray diffraction

Samples were ground into a fine powder and placed on low-background silicon wafer sample holders. PXRD experiments were performed using a PANalytical Empyrean diffractometer with a copper anode (wavelengths: $K_{\alpha1}$ = 1.5406 Å, $K_{\alpha2}$ = 1.5443 Å) and a Pixel 2D detector. The diffractometer did not have a monochromator fitted but the K_β radiation was removed with a nickel filter.

Elemental analysis

Elemental analysis data was collected using a Thermo Scientific FlashSmart CHNS Elemental analyser.

Raman spectroscopy

Samples were ground into a fine powder and placed on a glass slide. Raman spectroscopy measurements were collected using a Renishaw inVia Raman microscope with a green laser (wavelength of 532 nm) at 10 % power for 10 accumulations for each sample. Deconvolution of the resulting spectra was performed using Voigt peak shapes.

Transmission electron microscopy

Small portions of sample (≈ 50 mg) were dispersed in ethanol (≈ 1 ml) by sonication for 10 min. One drop of the dispersion was pipetted on to a carbon-coated copper TEM grid. TEM imaging was performed using Jeol (Japan) JEM 1400, at an acceleration voltage of 80 kV and magnification ranging between 400x and 40,000x. Imaging and size analysis was performed using the AMT XR60 12MPx CCD camera and its AMT camera software.

Small angle X-ray scattering

Samples were ground into a fine powder and distributed across a hole in a paper sample holder between two pieces of Scotch® Magic™ tape. The wide-range SAXS experiments were performed using the Multi-scale Analyser for Ultrafine Structures (MAUS) at the Federal Institute for Materials Research and Testing (BAM), Berlin. Copper and molybdenum anodes (8 eV and 17 eV photons, respectively) were used to measure over a wide q-range.

Nitrogen sorption

Nitrogen sorption measurements were carried out at 77 K using a Quantachrome Nova 1000 series volumetric gas sorption analyser. 50-200 mg of sample was degassed at 150 °C for 24 hr under vacuum. Isotherms were collected with filler rods over the range p/p_0 0.015 – 0.95. BET surface areas were calculated by applying the Rouquerol correction to select an appropriate p/p_0 range using the method recommended by the International Organization for Standardization (ISO) 9277.[1] The total pore volume measurable by nitrogen sorption was obtained from the isotherm plateau at p/p_0 0.95 and the micropore volume and micropore surface area was calculated using the *t*-plot method, according to ISO 15901-3.[2]

Thermogravimetric analysis

TGA data was obtained using a Q50 - Thermogravimetric Analyzer (TA instruments). Thermograms were recorded under an N_2 atmosphere at a heating rate of 10 $\mathrm{Kmin^{-1}}$, from 25-800 °C, with an average sample weight of ca. 10 mg.

Thermogravimetric analysis-Mass spectrometry

TGA-MS data was obtained using a NETZSCH STA 449F3 Jupiter instrument, the samples were run from 40-800 °C under a nitrogen atmosphere with a 10 Kmin-1 ramp rate.

X-ray photoelectron spectroscopy

XPS Analysis was performed using a Kratos Axis SUPRA XPS fitted with a monochromated Al kα X-ray source (1486.7 eV), a spherical sector analyser and 3 multichannel resistive plate, 128 channel delay line detectors. All data was recorded at 150W and a spot size of 700 x 300 µm. Survey scans were recorded at a pass energy of 160 eV, and high-resolution scans recorded at a pass energy of 20 eV. Electronic charge neutralization was achieved using a magnetic immersion lens. Filament current = 0.27 A, charge balance = 3.3 V, filament bias = 3.8 V. All sample data was recorded at a pressure below 10-8 Torr and at 298 K temperature. Data was analysed using CasaXPS[3] v2.3.20PR1.0 and the spectra were calibrated with C1s peak at 284.8 eV.

Results and Discussion

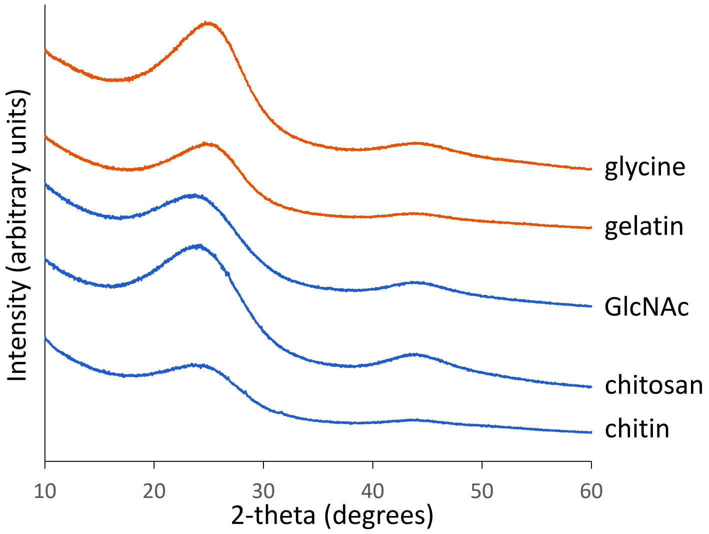

Figure S1 XRD patterns for control carbons synthesized by pyrolysis of nitrogen-rich precursors without any iron catalyst.

Table S1 Fitting values for Raman spectra for carbon samples produced from glycine, gelatin, N-acetylglucosamine, chitosan and chitin (5 g) and iron nitrate solution (0.68 mmol), held at 800 °C for 1 h. All measurements were collected in triplicate on different locations and the average values are reported with uncertainty values.

Precursor	Band	Peak centre (cm^{-1})	FWHM (cm^{-1})	I_{D1}/I_G
Glycine	G	1595 +/- 2	93 +/- 5	1.18 +/- 0.08
	D1	1357 +/- 4	167 +/- 17	
Gelatin	G	1599 +/- 1	92 +/- 2	1.24 +/- 0.04
	D1	1358 +/- 1	176 +/- 7	
N-acetylglucosamine	G	1585 +/- 2	78 +/- 2	1.32 +/- 0.01
	D1	1336+/- 1	127 +/- 7	
Chitosan	G	1591 +/- 3	81 +/- 5	1.31 +/- 0.03
	D1	1344 +/- 3	136 +/- 22	
Chitin	G	1587 +/- 1	91 +/- 1	1.04 +/- 0.01
	D1	1345 +/- 2	163 +/- 4	

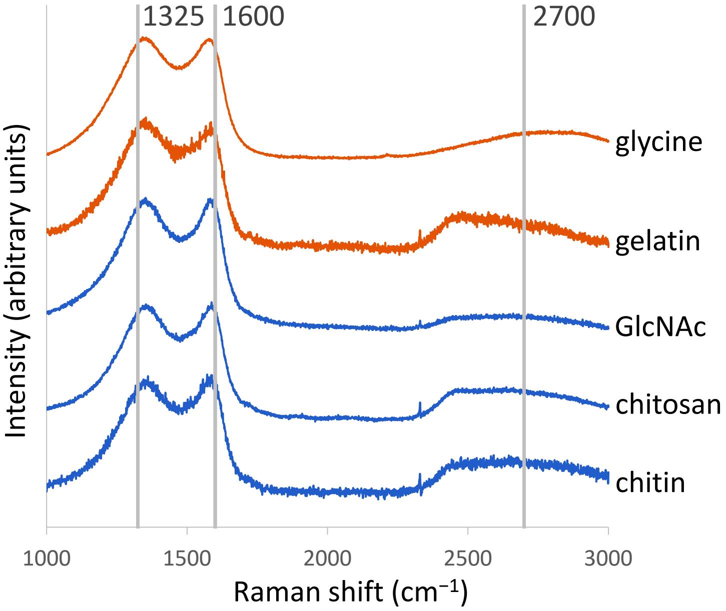

Figure S2 Raman spectra for control carbons synthesized by pyrolysis of nitrogen-rich precursors without any iron catalyst.

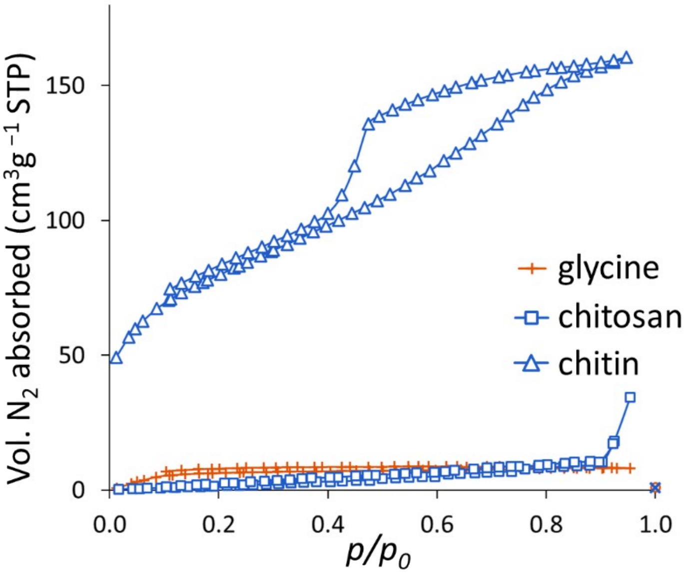

Figure S3 Porosimetry data for control samples.

Table S2 Adsorptive properties of carbons produced from glycine, gelatin, GlcNAc, chitosan and chitin (5 g) and iron nitrate (0.67 mmol).

Precursor	S_{BET} ($m^2 g^{-1}$)	Max Q_{ads} ($cm^3 g^{-1}$)	V_{tot} ($cm^3 g^{-1}$)	S_{micro} ($m^2 g^{-1}$)	V_{micro} ($cm^3 g^{-1}$)
Glycine	26	9	0.013	7	0.001
Chitosan	12	35	0.050	0	0
Chitin	290	160	0.25	57	0.023

Table S3 Elemental analysis of N-doped carbons prepared from from N-containing organic precursors (5 g) and iron nitrate (0.67 mmol). Values are listed as a % of the total mass.

Precursor	C%	H%	N%	Residual mass %
Glycine	71	1	15	13
Gelatin	70	4	14	13
N-acetylglucosamine	80	1	5	14
Chitosan	82	1	9	8
Chitin	79	1	6	14

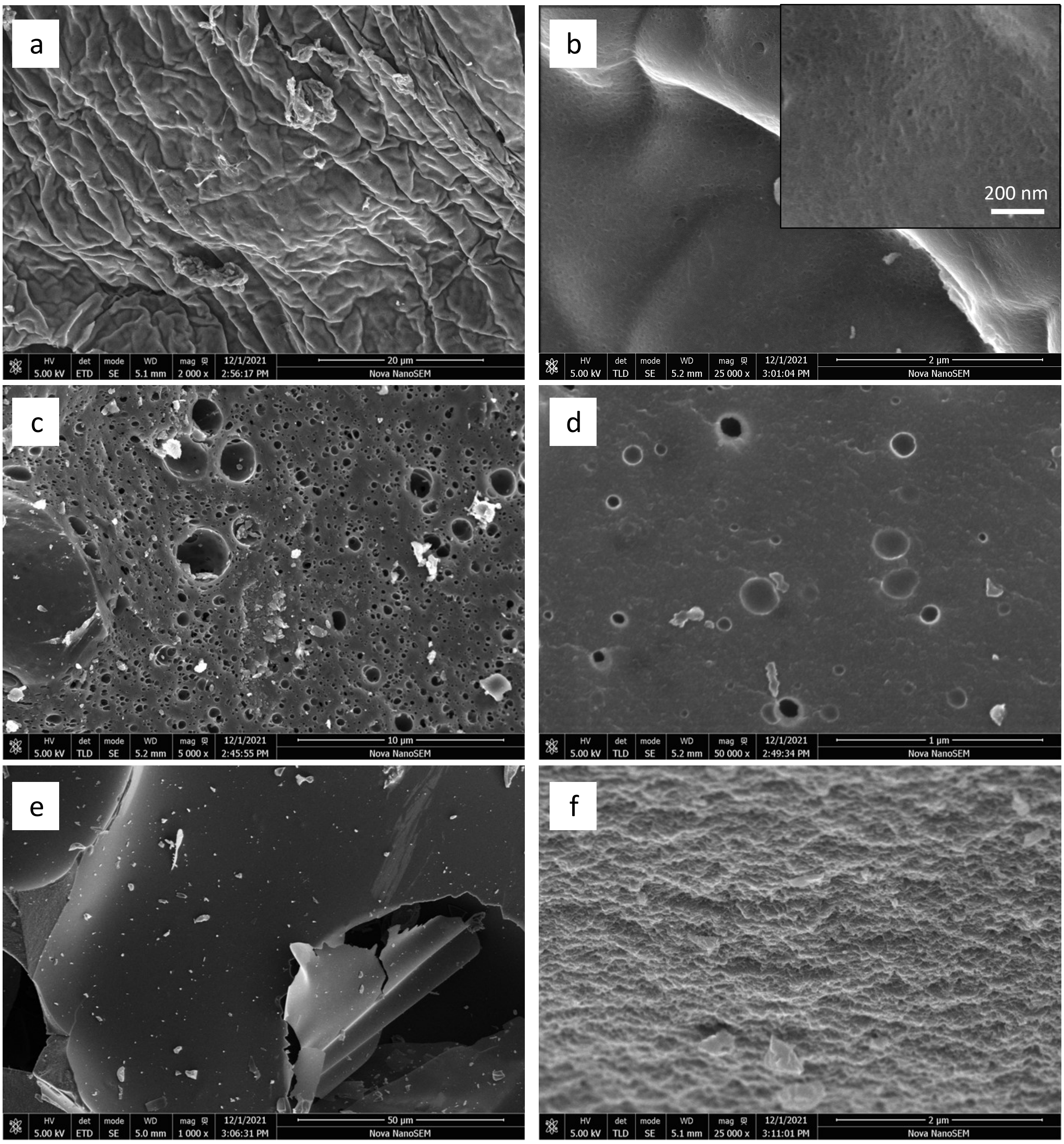

Figure S4 SEM images of a/b) chitin-derived carbon, c/d) chitosan-derived carbon and e/f) GlcNAc-derived carbon. Inset of figure S4b shows a magnification of the image, with very small pores visible.

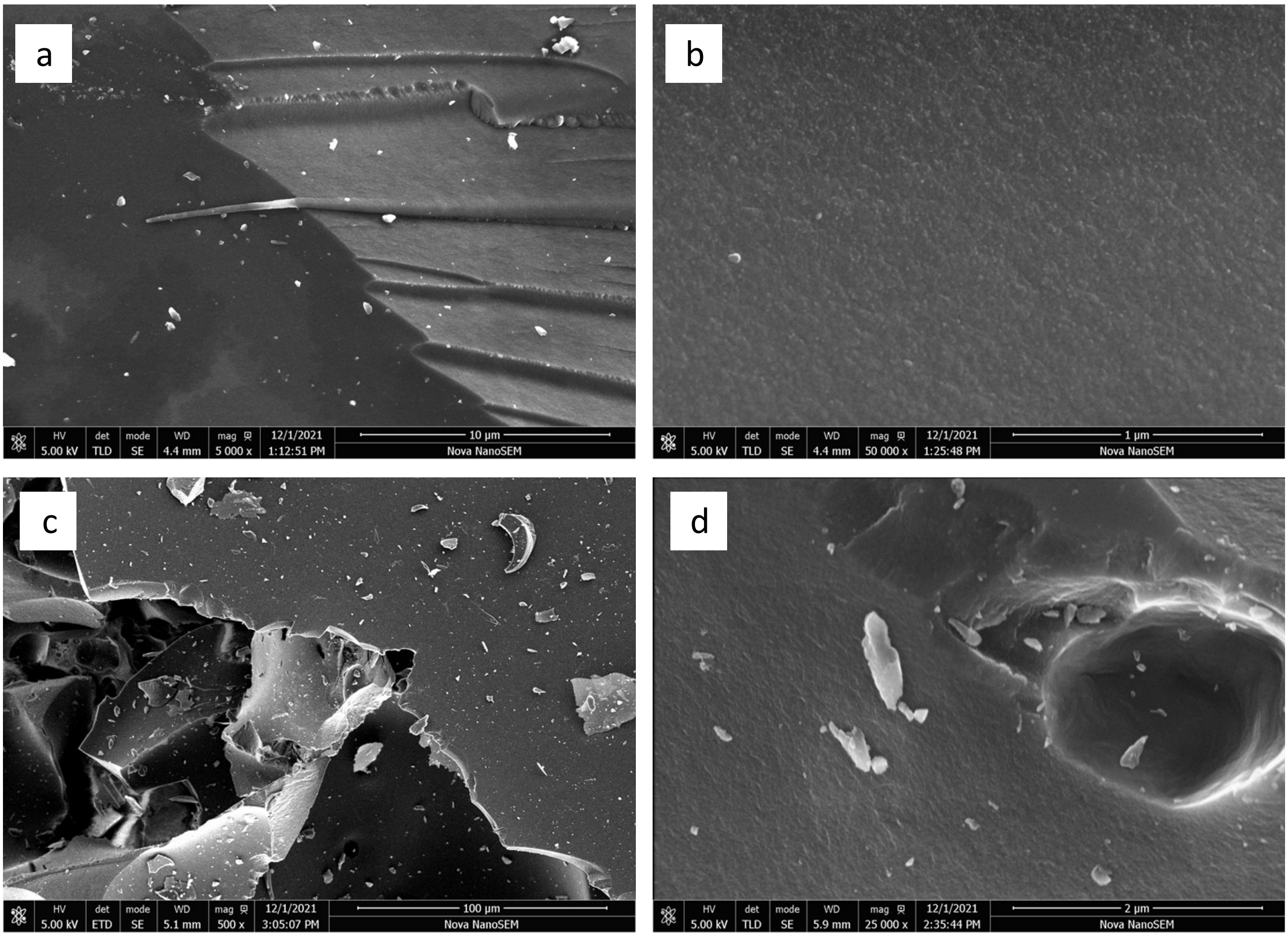

Figure S5 SEM images of a/b) gelatin-derived carbon, c/d) glycine-derived carbon.

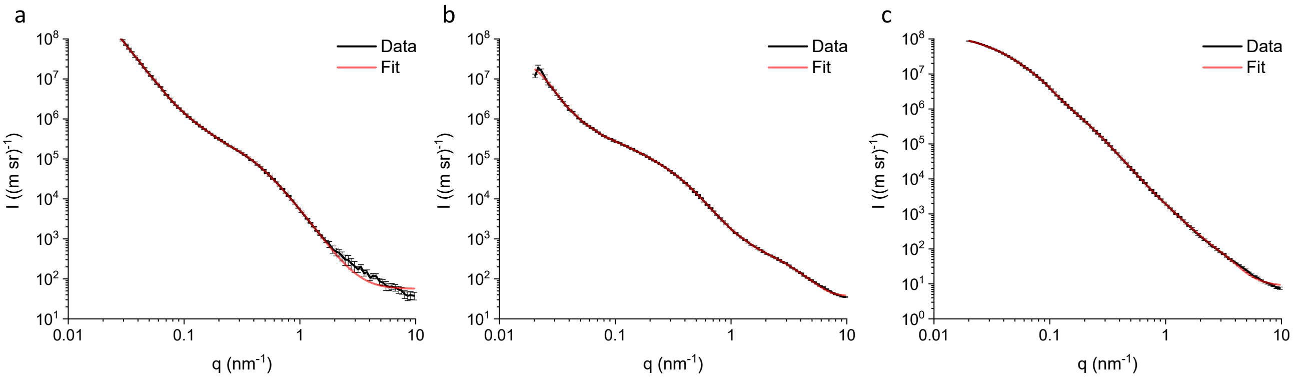

Figure S6 Raw SAXS data vs McSAS fits for a) chitin, b) chitosan, and c) GlcNAc-derived carbons.

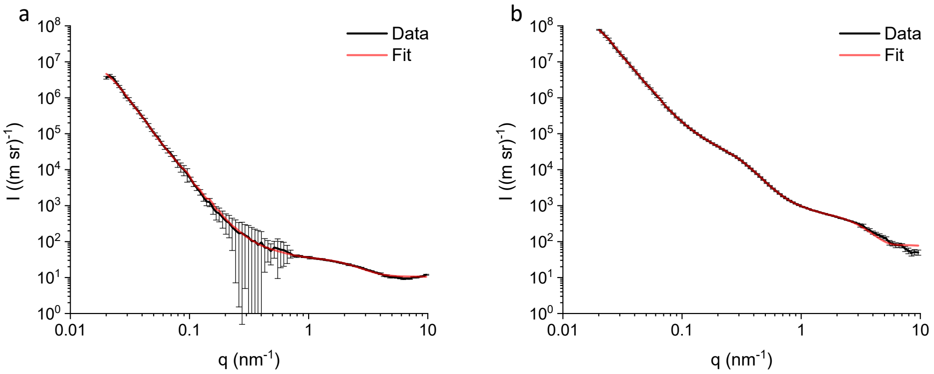

Figure S7 Raw SAXS data vs McSAS fits for a) gelatin, and b) glycine-derived carbons.

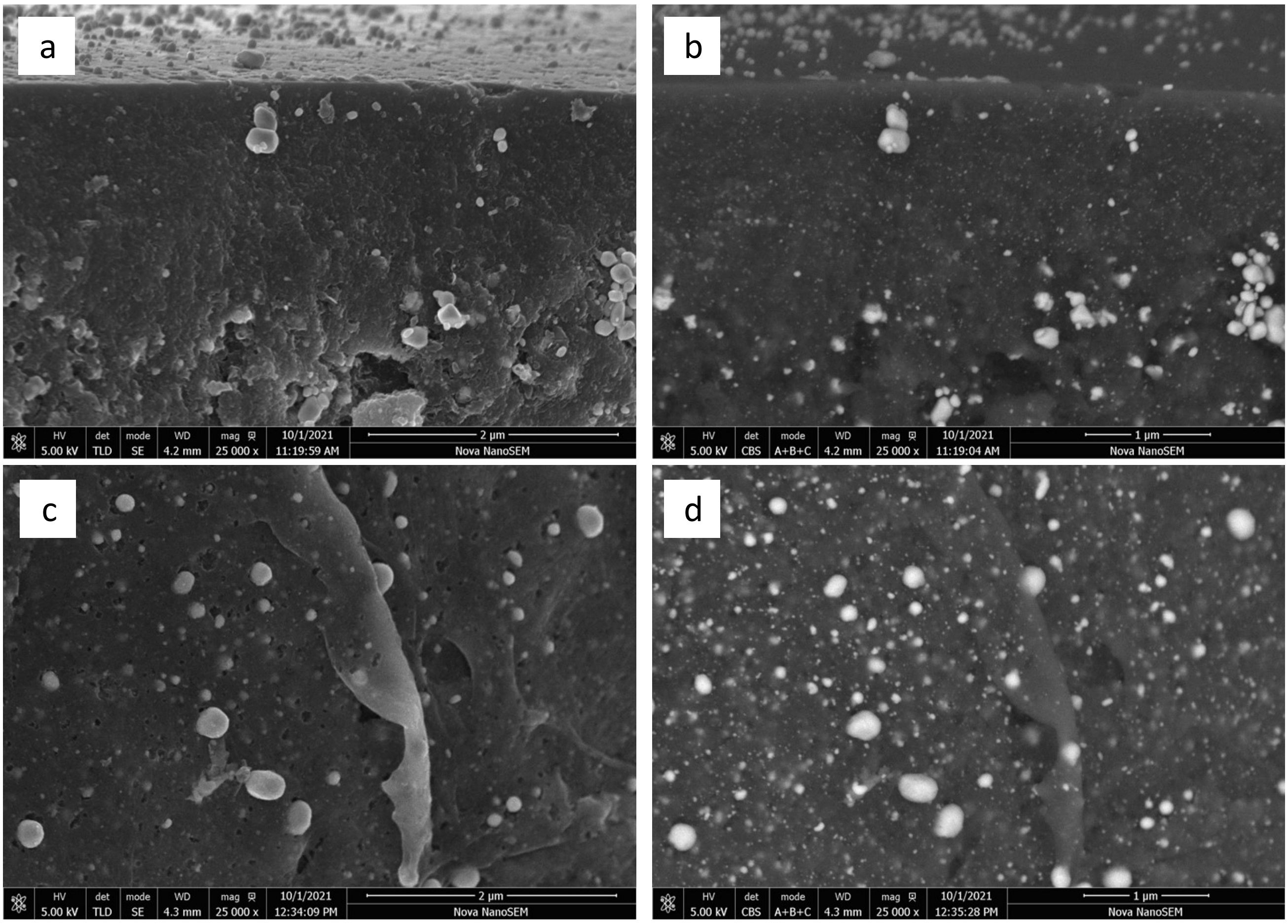

Figure S8 SEM images of carbons prepared using 3.3 mmol of $Fe(NO_3)_3$ per 5 g of biomass. Images show chitin derived carbon with a) secondary electron and b) backscattered electron detectors and gelatin-derived carbon with a) secondary electron and b) backscattered electron detectors.

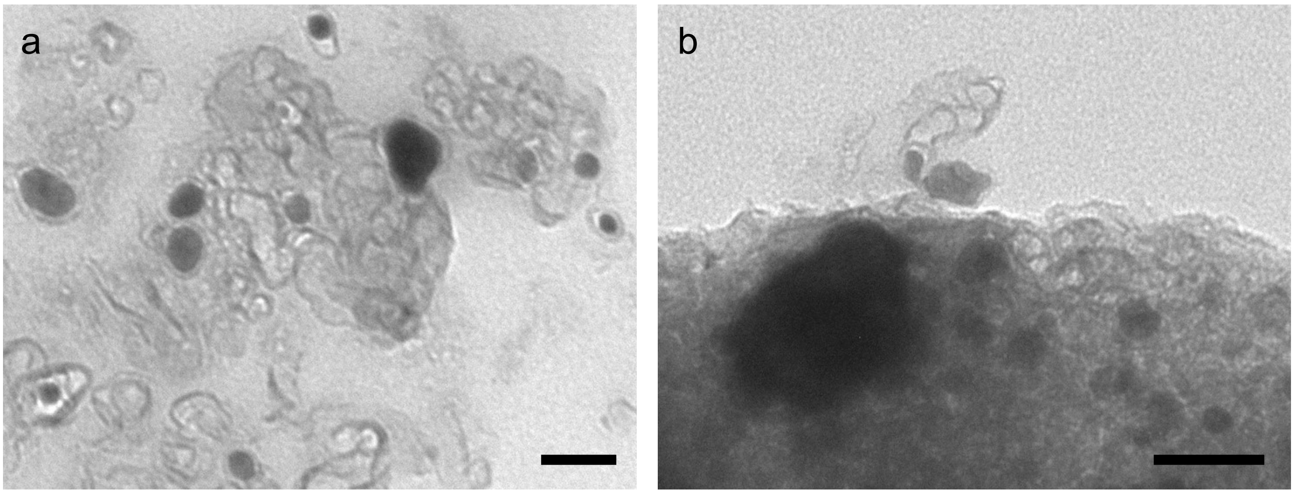

Figure S9 TEM images of porous carbons prepared by pyrolysis of $Fe(NO_3)_3$ (3.3 mmol) with 5 g of a) chitin and b) gelatin. Scale bar = 50 nm.

Table S4 Adsorptive properties of carbons produced from glycine, gelatin, GlcNAc, chitosan and chitin (5 g) and iron nitrate (3.3 mmol).

Precursor	S_{BET} ($m^2\,g^{-1}$)	Max Q_{ads} ($cm^3\,g^{-1}$)	V_{tot} ($cm^3\,g^{-1}$)	S_{micro} ($m^2\,g^{-1}$)	V_{micro} ($cm^3\,g^{-1}$)
Glycine	180	85	0.13	56	0.023
Gelatin	410	180	0.27	160	0.06
GlcNAc	250	130	0.20	83	0.036
Chitosan	360	200	0.31	130	0.055
Chitin	370	220	0.34	79	0.036

Table S5 Elemental analysis of N-doped carbons prepared from from N-containing organic precursors (5 g) and iron nitrate (3.3 mmol). Values are listed as a % of the total mass.

Precursor	C%	H%	N%	Residual mass %
Glycine	67	1	6	26
Gelatin	74	1	2	23
N-acetylglucosamine	75	0	1	23
Chitosan	72	0	1	26
Chitin	76	0	1	23

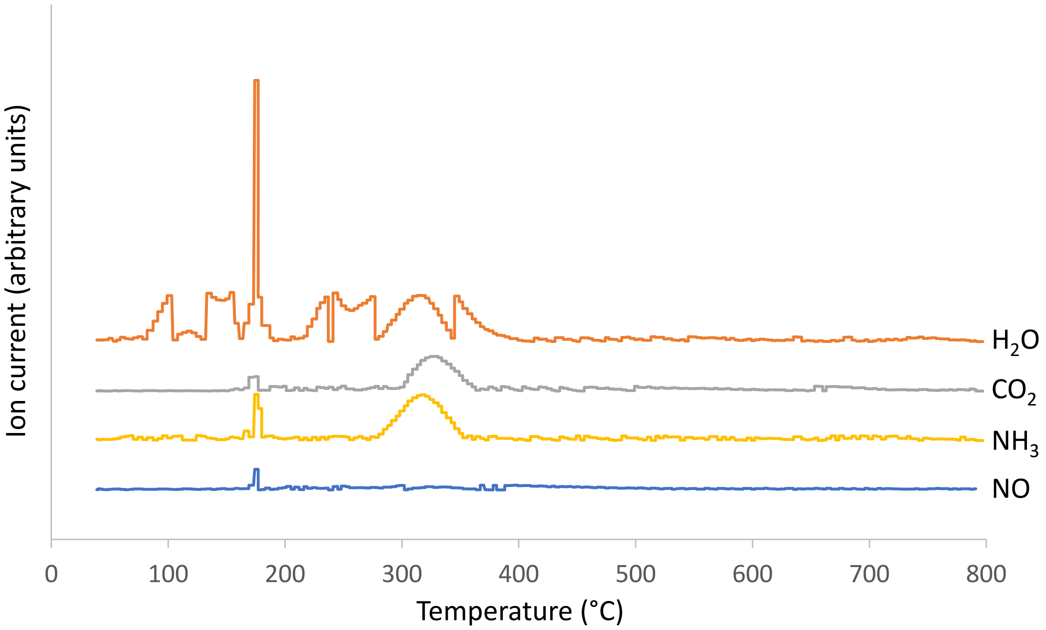

Figure S10 Mass spectrometry data from TGA-MS measurements of gelatin (5 g) and iron nitrate (3.3 mmol).

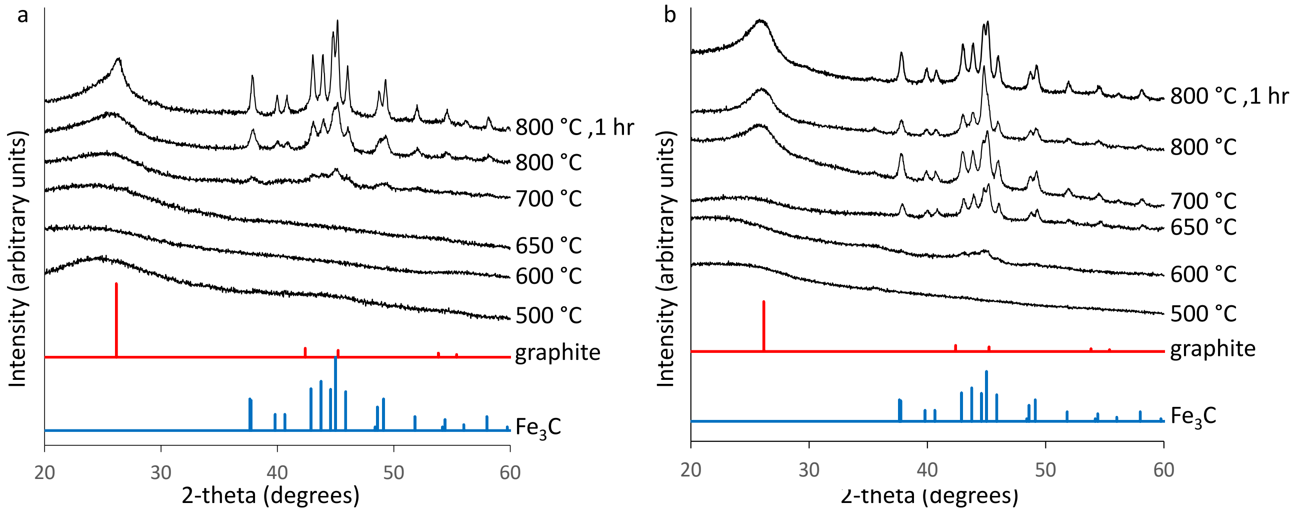

Figure S11 XRD data for carbons derived from 5 g of a) gelatin and b) chitin with 3.3 mmol of $Fe(NO_3)_3$ under various heating conditions.

Table S6 Elemental analysis of carbons prepared from gelatin (5 g) and iron nitrate (3.3 mmol) at various temperatures and hold times.

Temperature (°C) / hold time (h)	C%	H%	N%
800 / 1	74	0.61	2.3
800 / 0	73	1.0	3.3
700 / 0	58	1.3	12
650 / 0	56	1.6	15

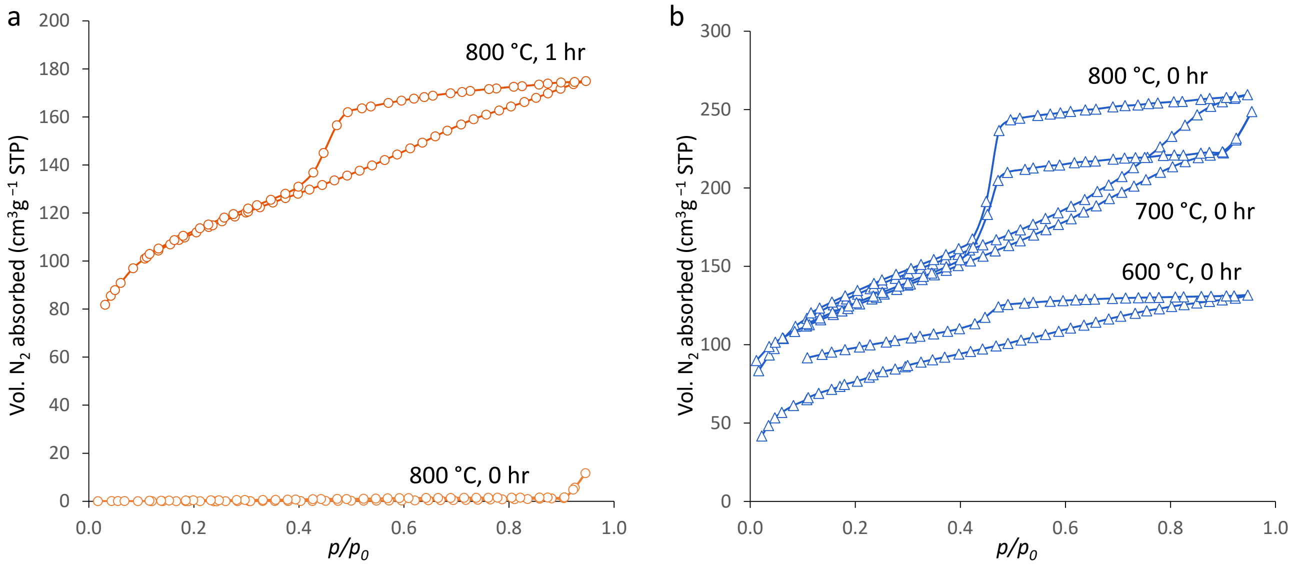

Figure S12 Porosimetry data for carbons derived from 3.3 mmol $Fe(NO_3)_3$ with 5 g of a) gelatin and b) chitin under various conditions

References

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[1] ISO. Determination of the Specific Surface Area of Solids by Gas Adsorption. BET Method. ISO 9277, 2010, pp. 1–24.

[2] ISO. Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption – Part 3: Analysis of micropores by gas adsorption. ISO 15901-3, 2007, pp. 1–27.

[3] N. Fairley, V. Fernandez, M. Richard-Plouet, C. Guillot-Deudon, J. Walton, E. Smith, D. Flahaut, M. Greiner, M. Biesinger, S. Tougaard, D. Morgan and J. Baltrusaitis, *Applied Surface Science Advances*, 2021, **5**, 100112.