

Supporting Information: Sol-Gel Preparation of Low Oxygen Content, High Surface Area Silicon Nitride and Imidonitride Materials

Kripasindhu Sardar,^a Richard Bounds,^a Marina Carravetta,^a Geoffrey Cutts,^b Justin S. J. Hargreaves,^c Andrew L. Hector,^{a,*} Joseph A. Hriljac,^b William Levason^a and Felix Wilson^a

^a Chemistry, University of Southampton, Southampton SO17 1BJ, UK. a.l.hector@soton.ac.uk

^b School of Chemistry, University of Birmingham, Birmingham B15 2TT, UK

^c School of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK

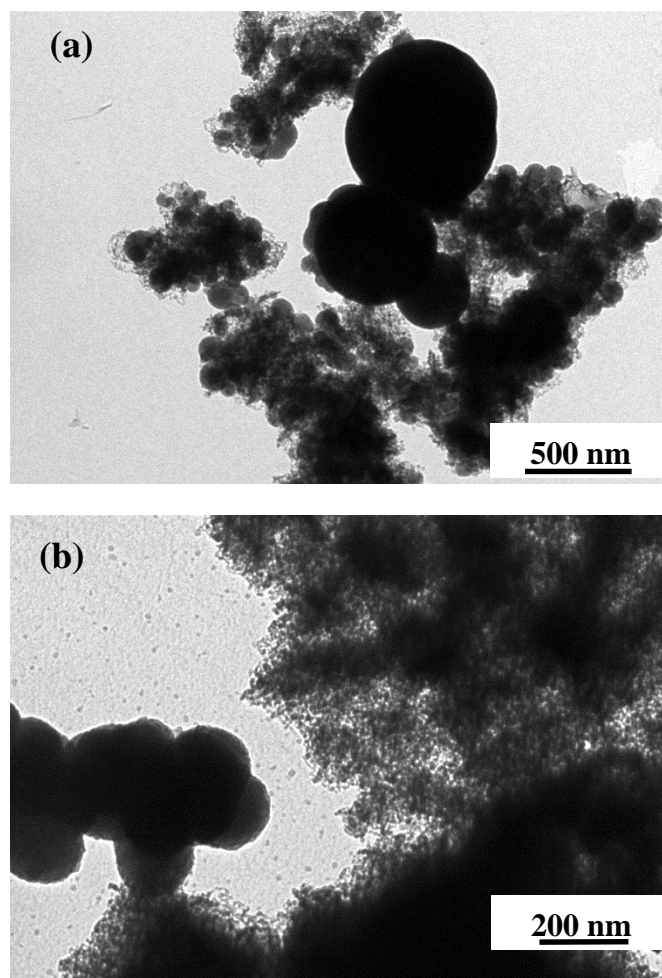


Fig. S1 Typical TEM images of silicon imidonitride samples prepared from (a) concentrated gel (5% $[\text{NH}_4][\text{OTf}]$, pyrolysis condition 200 °C/2 h + 1000 °C/2 h) and (b) dilute -gel (10% $[\text{NH}_4][\text{OTf}]$, 200 °C/2 h + 800 °C/2 h)

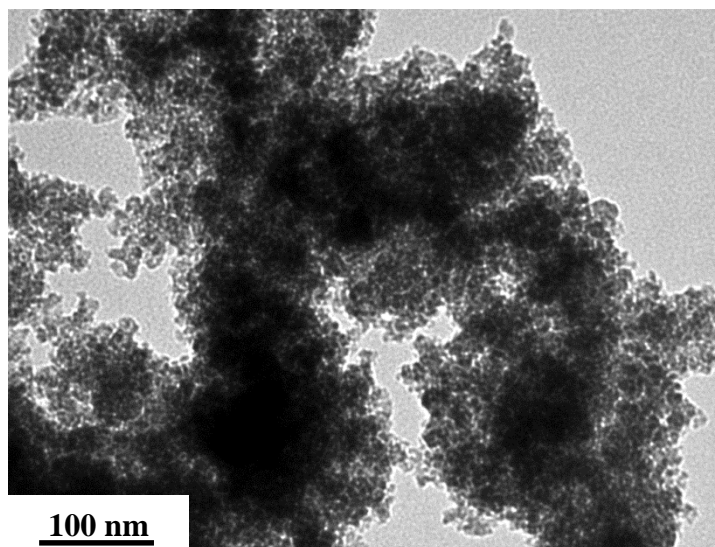


Fig. S2 Typical TEM image of silicon imidonitride prepared by heating a xerogel made with 0.4% $[\text{NH}_4][\text{OTf}]$ at 200 °C for 6 h under NH_3 .

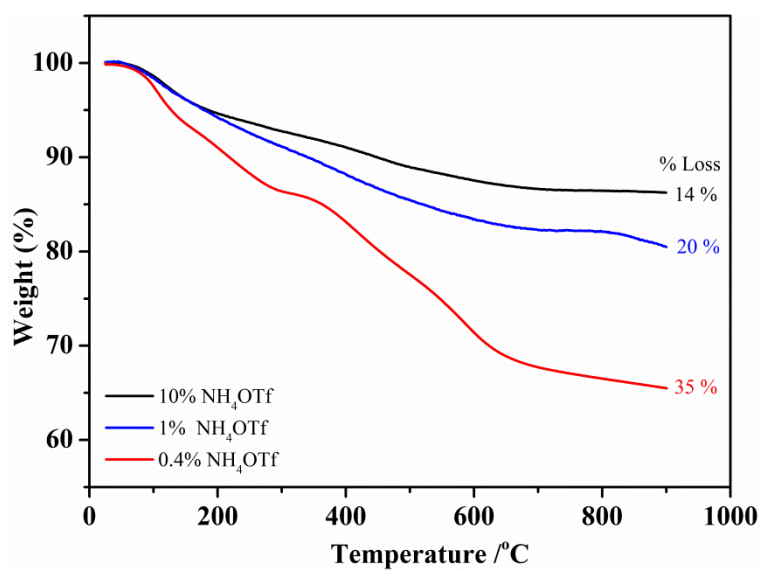


Fig. S3 TGA traces of silicon imidonitride xerogels prepared with varying ammonium triflate concentrations.

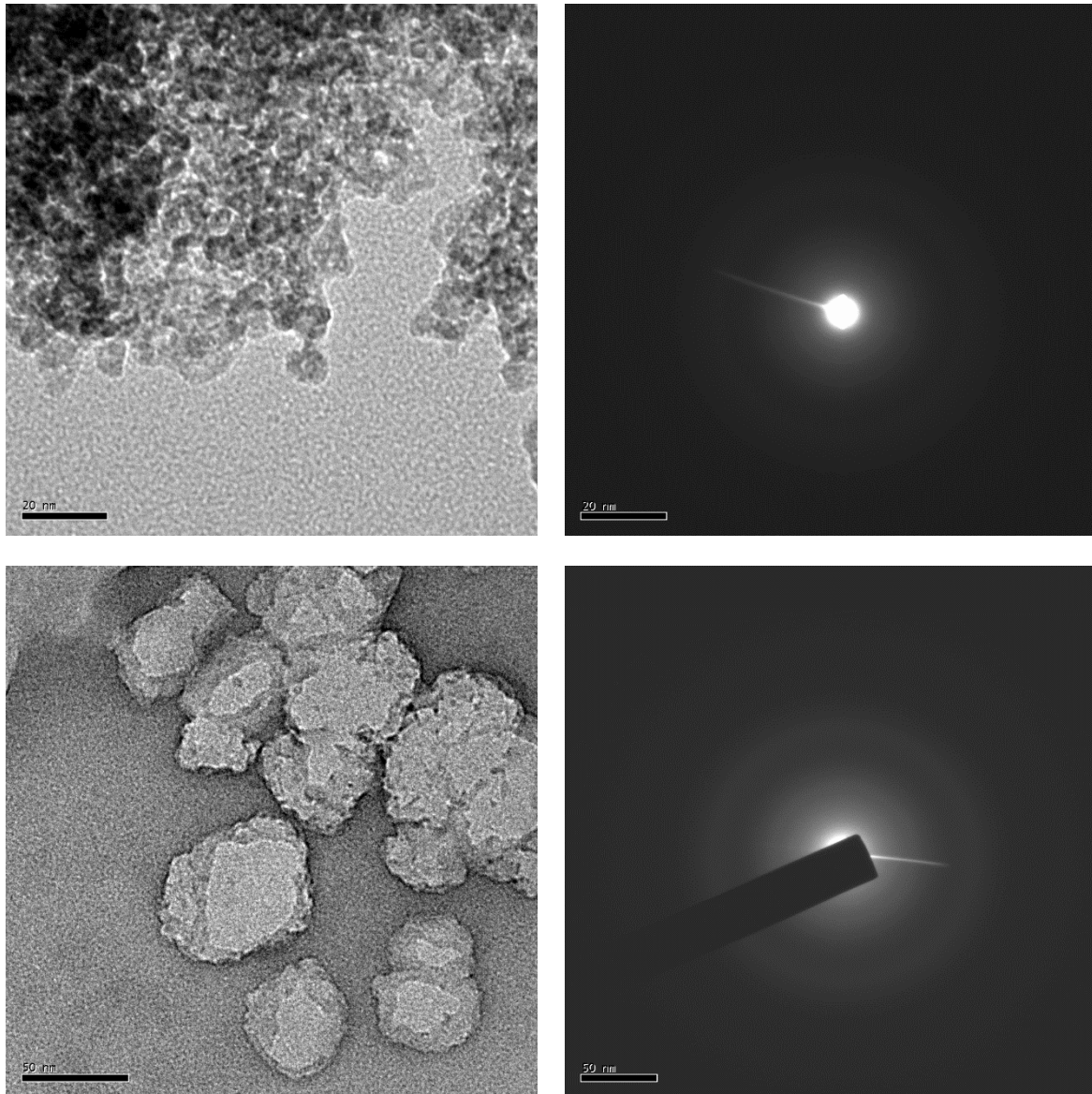


Fig. S4 TEM images (left) and selected area electron diffraction (right) of silicon imidonitride produced at 1200 °C (top) and amorphous regions of silicon imidonitride produced at 1400 °C (bottom).

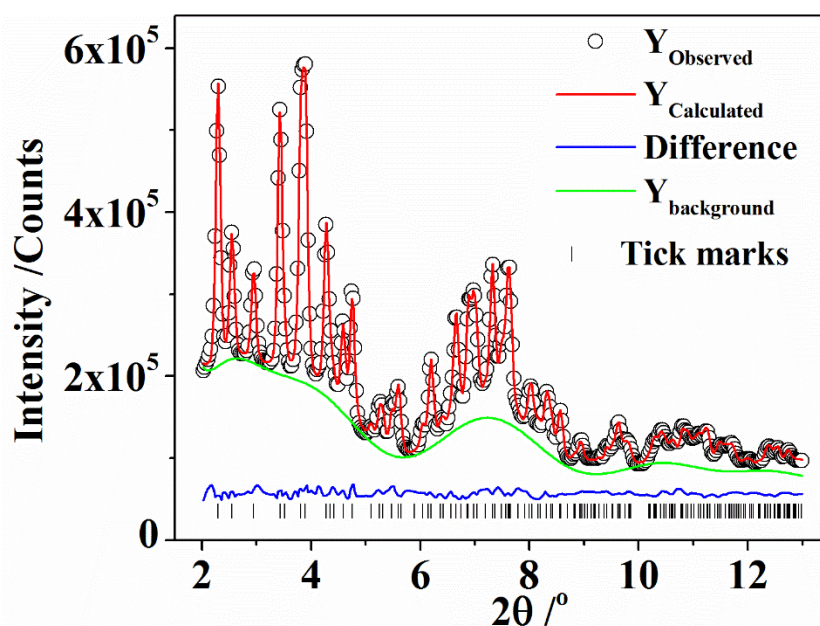


Fig. S5 Rietveld refinement of Bragg diffraction pattern ($\lambda = 0.1722 \text{ \AA}$, d spacing range $0.76\text{--}4.88 \text{ \AA}$, 2D image integrated with a step size of 0.0275°) of silicon imidonitride samples synthesised at $1400 \text{ }^\circ\text{C}/18 \text{ h}$ from a xerogel obtained with 0.4% $[\text{NH}_4][\text{OTf}]$. Tick marks correspond to $\alpha\text{-Si}_3\text{N}_4$ in space group $P31c$ (159) $R_{\text{wp}} = 1.84\%$ $R_p = 1.44\%$.

Table S1 Refined atomic coordinates of crystalline silicon nitride sample synthesised at $1400 \text{ }^\circ\text{C}$ for 18 h . Tick marks correspond to $\alpha\text{-Si}_3\text{N}_4$ in space group $P31c$ (159). Lattice parameters are $a = 7.7806(10) \text{ \AA}$ and $c = 5.6423(10) \text{ \AA}$. Unit cell volume $V = 295.81(8) \text{ \AA}^3$.

Atom	Wyckoff symbol	x	y	z	$U_{\text{iso}} \times 100$	Occupancy
Si1	6c	0.0810(6)	0.5135(6)	0.6570(14)	1.33(9)	1
Si2	6c	0.2551(5)	0.1672(5)	0.4539(14)	1.33(9)	1
N1	6c	0.6478(12)	0.6108(13)	0.420(3)	0.41(13)	1
N2	6c	0.3100(13)	0.3196(12)	0.712(3)	0.41(13)	1
N3	2b	0.3333	0.6667	0.614(3)	0.41(13)	1
N4	2a	0.0000	0.0000	0.452(4)	0.41(13)	1

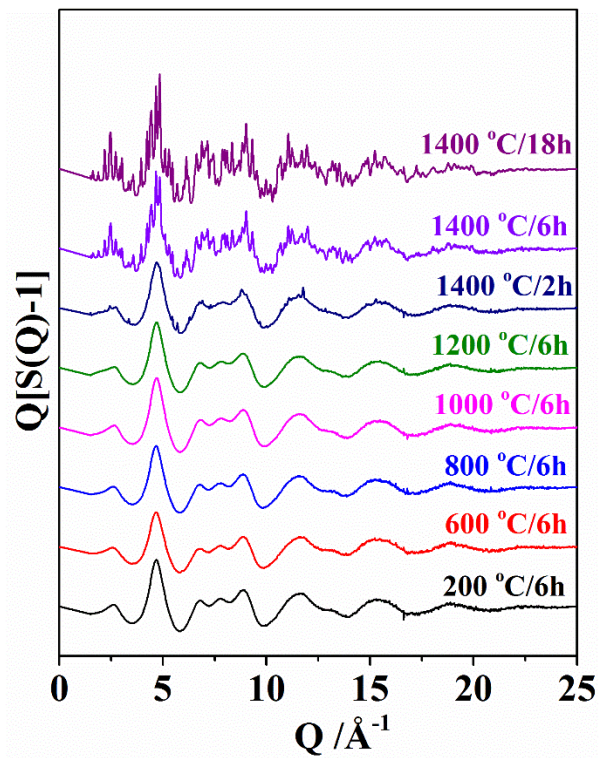


Fig. S6 Reduced total scattering structure function $F(Q)$ defined as $Q[S(Q)-1]$ derived from diffraction patterns of samples prepared by nitridation within a temperature range of 200-1400 °C. Patterns have been equally offset along the Y axis.

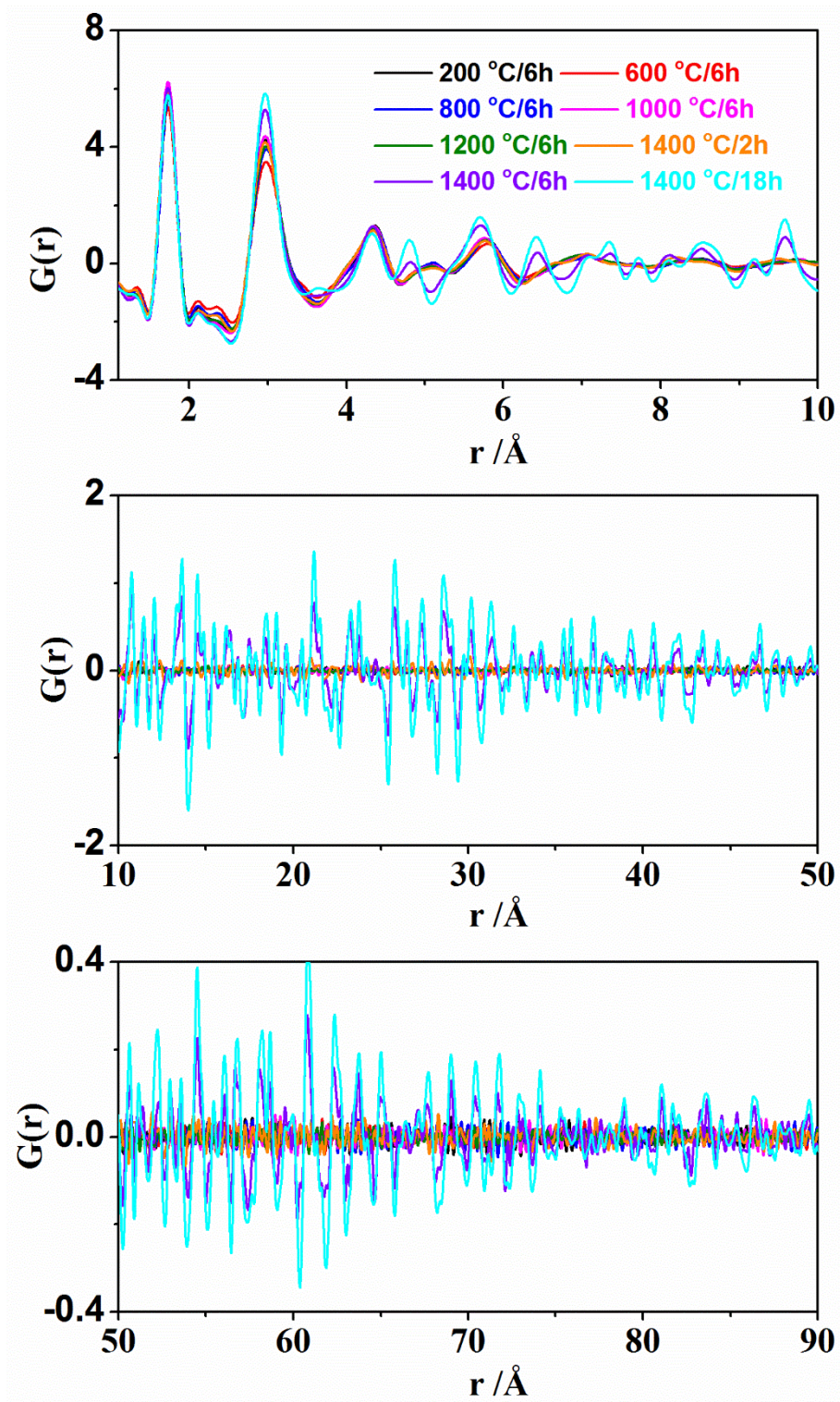


Fig. S7 Pair distribution function $G(r)$ for silicon imidonitride samples prepared within a temperature range of 200-1400 °C shown in three different r regions.

Table S2 Summary of PDFGUI refined parameters for the silicon imidonitride sample synthesised at 1400 °C for 18 h

Q_{damp}	0.146(12)
a / Å	7.763(14) Å
c / Å	5.609(17) Å
Scale factor	0.96(4)
delta2	1.9(2)
S_{ratio}	1.3(3)
N_{uiso}	0.0059(19)
Si_{uiso}	0.0033(11)
R_w	0.20611
Reduced χ^2	0.0928898

In order to account for correlated motion Delta2 was initially refined and then S_{ratio} was refined with a Rcut value of 10 Å (the full data range).

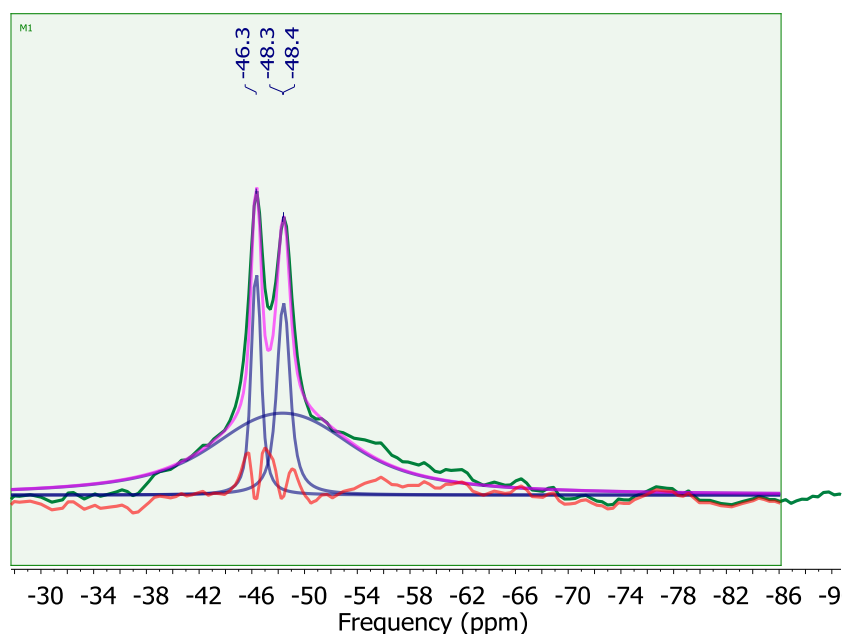


Fig. S8 ²⁹Si MAS-NMR peak deconvolution of silicon imidonitride sample synthesised at 1400 °C for 18 h. The sharp crystalline peaks are at 46.3 and 48.4 ppm and the broad amorphous peak at 48.3 ppm. The difference between the measured and modelled spectra is shown in red.

Table S3 Results from fitting of NMR spectra (note a, b refers to two sharp peaks, c is a broad component)

Cross polarisation data						
	#	ppm	Height	Width(Hz)	L/G	Area
600C /6h	1	-42.6	5818619.8	1249	1.67	363153264
800C /6h	2	-44.3	6183609.2	1390	1.59	435389284
1000C /6h	3	-47	5850103.8	1772	2	488208166
1200C /6h	4	-46.8	5854589.5	1742	2	480266214
1400C/2h	5	-47.3	5809316.5	1813	2	496129536
1400C/6h	6	-47.2	5491038.8	1942	2	502150110
1400C/18h	7a	-47.4	4906927.8	1988	1.55	497121782
1400C/18h	7b	-45				
One pulse data						
	#	ppm	Height	Width(Hz)	L/G	Area
1000C/6h	1	-47.4	1668.2	1808	2	142051.97
1200C/6h	2	-48.7	1662.41	1707	2	133687.12
1400C/2h	3	-48.3	1601.09	1596	2	120375.66
1400C/6h	4a (Sharp Component)	-46.6	818.95	148	1	6768.224
1400C/6h	4b (Sharp component)	-48.7	812.47	137	0.68	6523.286
1400C/6h	4c (Broad component)	N/A	859.15	2063	0.79	101899.7
1400C/18h	5a (Sharp component)	-46.3	1372.24	107	0.96	8204.346
1400C/18h	5b (Broad component)	N/A	450.41	1515	0.58	40463.565
1400C/18h	5c (Sharp component)	-48.4	1214.37	141	0.6	10125.023