Supporting information

Low temperature nitridation of Fe_3O_4 by reaction with $NaNH_2$

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Collection Code	Space Group	Formula	Volume ($Å^3$)	Temperature (K)	Year	Quality Data	DOI
79982	$P6_322$	Fe_3N	84.24	298	1995	*	10.1016/0925-8388(95)01610-4
79983	$P6_322$	Fe_3N	83.71	295	1995	*	10.1016/0925-8388(95)01610-4
80930	$P6_322$	Fe_3N	83.63	293	1995	*	No DOI
93173	$P6_322$	$Fe_3N_{1.107}$	84.48	293	2001		10.1016/S0925-8388(00)01435-3
93174	$P6_322$	$Fe_3N_{1.239}$	85.69	293	2001		10.1016/S0925-8388(00)01435-3
93175	$P6_322$	$Fe_3N_{1.3}$	86.63	293	2001		10.1016/S0925-8388(00)01435-3
93176	$P6_322$	$Fe_3N_{1.33}$	87.05	293	2001		10.1016/S0925-8388(00)01435-3
93177	$P6_322$	$Fe_3N_{1.39}$	87.60	293	2001		10.1016/S0925-8388(00)01435-3
93183	$P6_322$	$Fe_3N_{1.1}$	84.49	293	2001		10.1016/S0925-8388(00)01435-3
93195	$P6_322$	$Fe_3N_{1.235}$	85.59	293	2001		10.1016/S0925-8388(00)01435-3
162698	$P6_322$	$Fe_3N_{1.2}$	84.77	293	2009		10.1021/cm802721k
163929	$P6_322$	$Fe_3N_{0.97}$	83.00	293	2009	*	10.1016/j.jallcom.2008.09.178
420214	$P6_322$	$Fe_3N_{1.47}$	88.39	293	2009	*	10.1002/ejic.200801222

Table S1: Cell volume and formula data for ε-$Fe_{2+x}N$ mined from the ICSD [28] and used to build the calibration and subsequent stoichiometry estimation shown in Figure S1. Note – quality data highlights with an asterisk data considered to be of highest quality by ICSD.

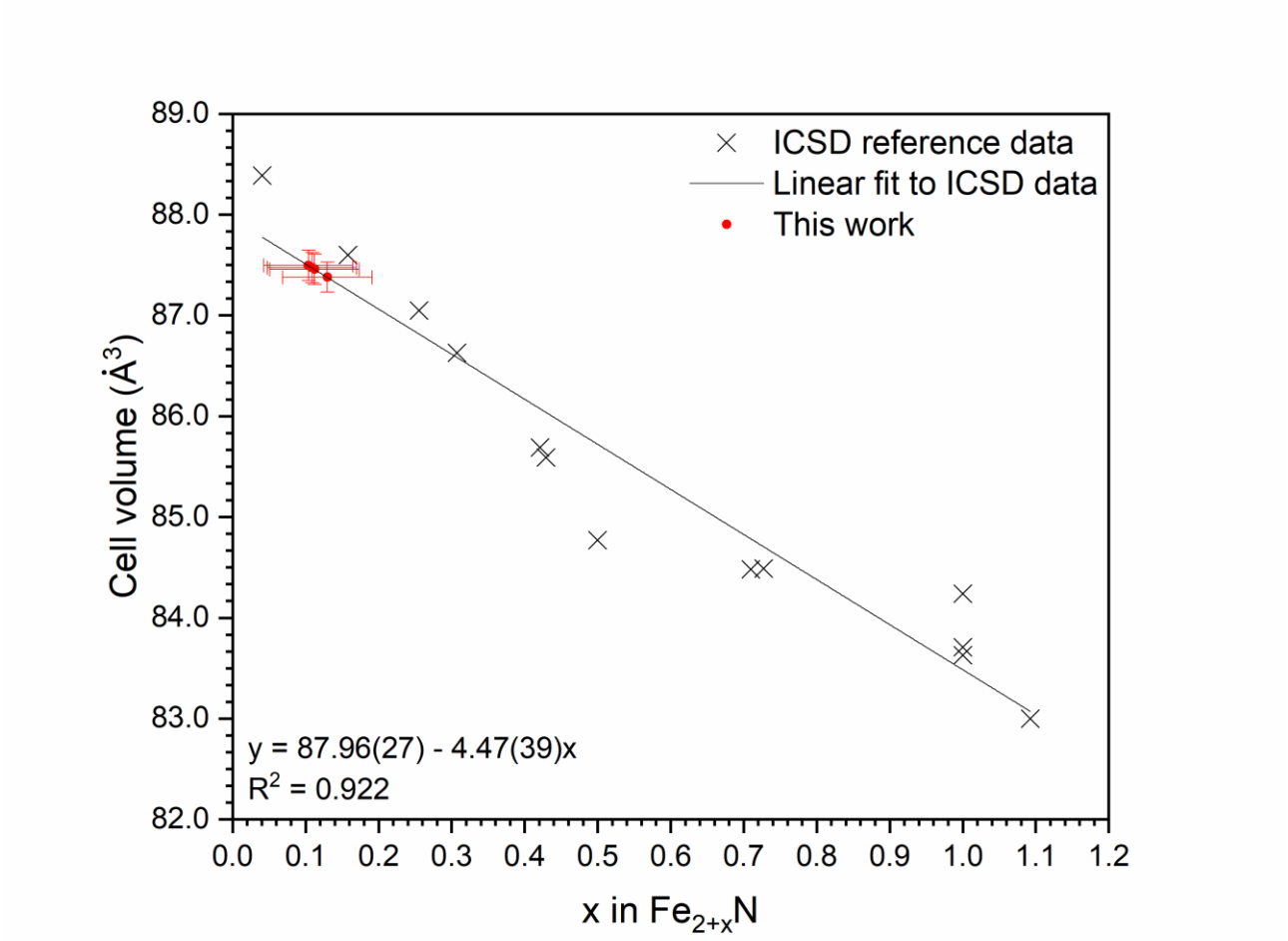

Figure S1: Dependence of unit cell volume on stoichiometry *x* in ***ε***-$Fe_{2+x}N$ assuming a linear dependence. Black crosses indicate data for *P*$6_3$22 ***ε***-$Fe_{2+x}N$ data sourced from the ICSD (Table S1), normalised to the $Fe_{2+x}N$ composition. The applied linear fit was then used to calculate the estimated *x* values for the data points in this work shown in red.

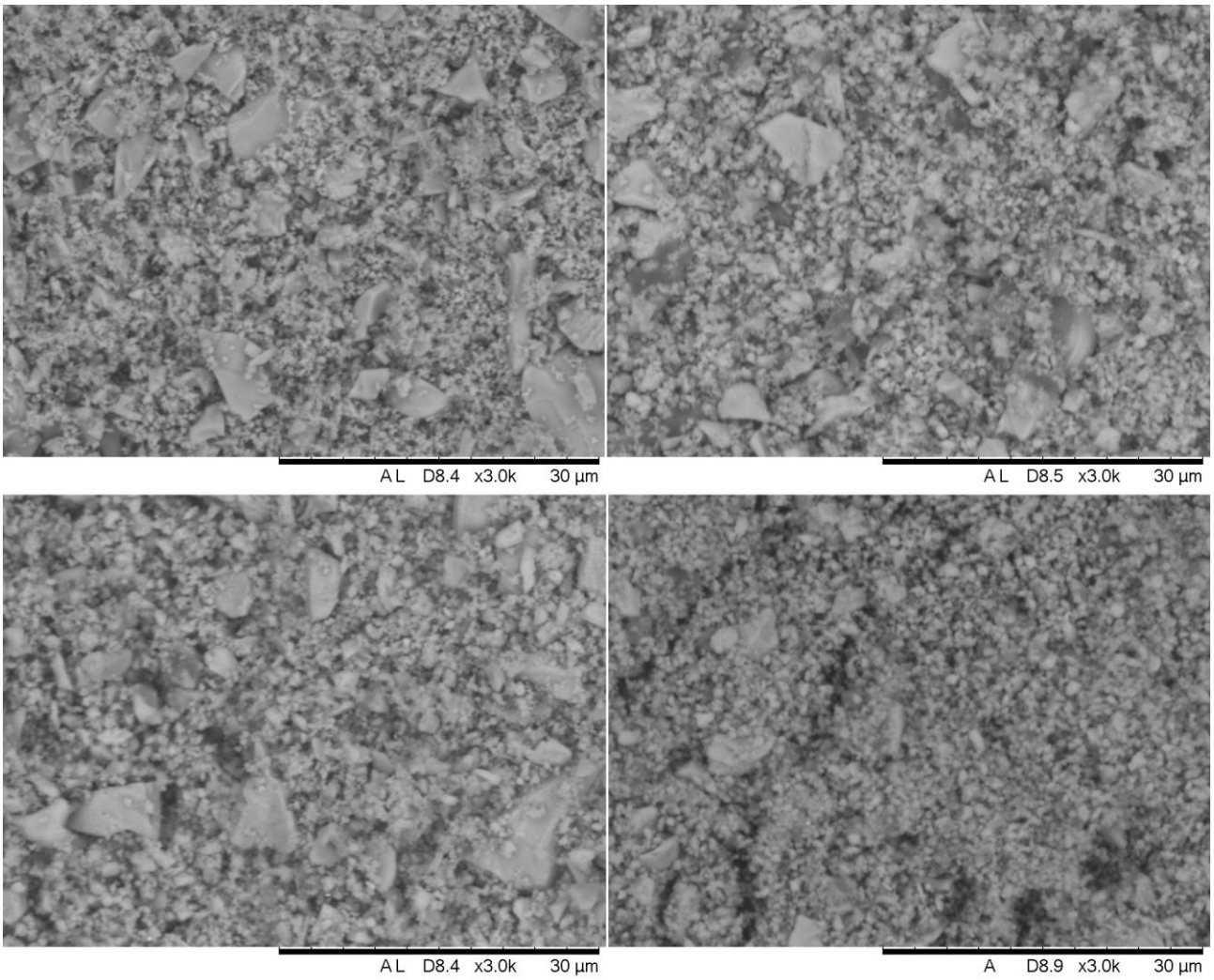

Figure S2: SEM images of raw and Fe_3O_4 powders reacted with $NaNH_2$ at 170 °C for 24, 48 and 96 h. Top row L-R: untreated Fe_3O_4, 24 h product. Bottom row L-R: 48 h product, 96 h product.

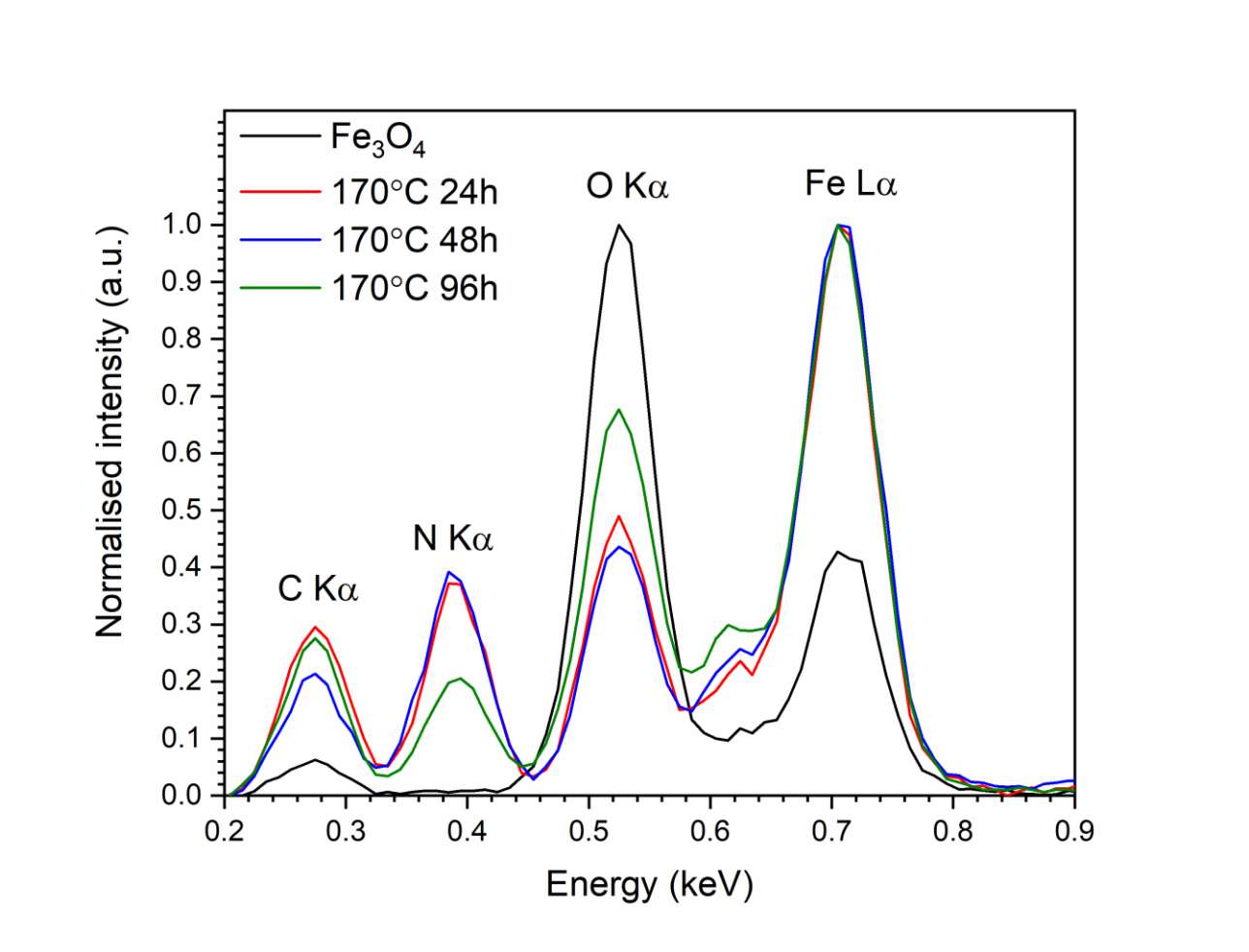

Figure S3: EDX spectra for starting Fe_3O_4 reagent (black) and products of amide reactions at 170 °C for 24 / 48 / 96 h (red/blue/green). Note the presence of N K*α* emission only in the reaction products. C K*α* emission is attributed to the adhesive tab used for securing the powder during SEM measurement.

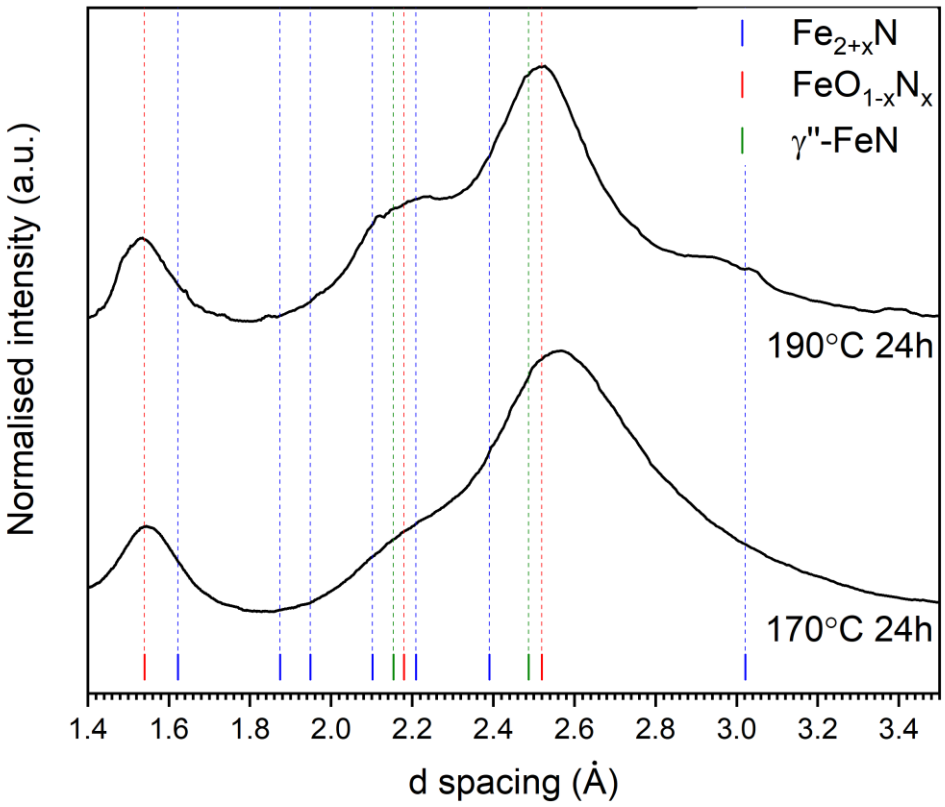

Figure S4: d spacing data integrated from electron diffraction linescans for (bottom) 170 °C / 24 h and (top) 190 °C / 24 h samples. Indexed are allowed reflections for ε-$Fe_{2+x}N$ (blue), $FeO_{1-x}N_x$ (red) and γ''-FeN (green) confirming the findings from recrystallisation data of the presence of the oxynitride and nitride phases.

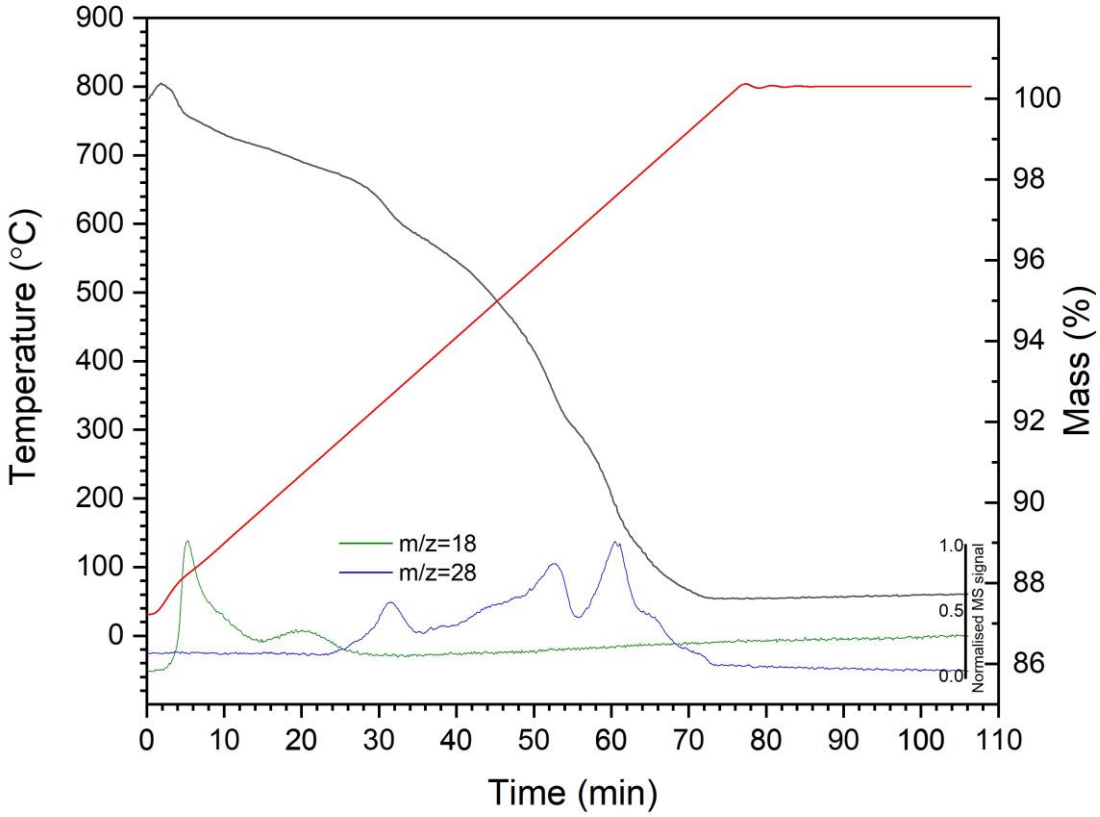

Figure S5: Thermogravimetry (TG, black) curve and mass spectrometry (MS) signals of 190 °C / 24 h product (mass numbers 18 and 28 represent H_2O and N_2).