Supporting information

Nitrogen adsorption and desorption at iron pyrite FeS$_2${100} surfaces

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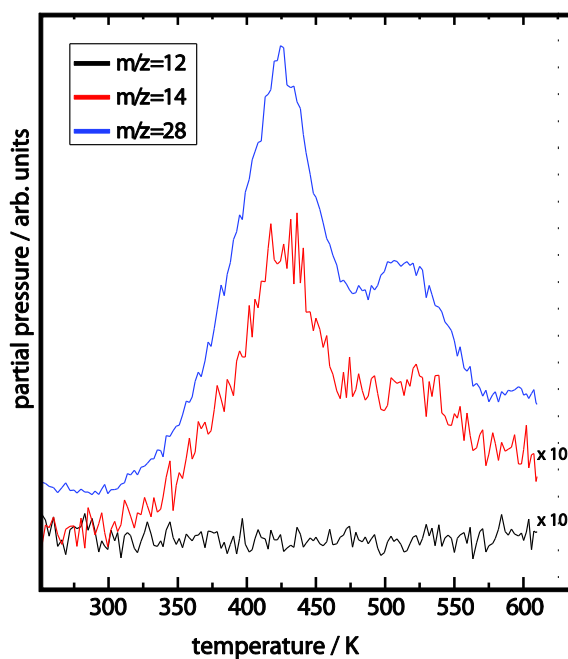
Figure S1: Examples of desorption spectra (without baseline correction) of m/z = 12, 14 and 28 after exposure to activated nitrogen, with a sample bias of +600 V. The absence of any feature in the m/z = 12 spectrum, together with the presence of matching features in the m/z = 28 and m/z = 14 spectra, confirms that the desorption features correspond to molecular nitrogen (N$_2$) rather than CO.
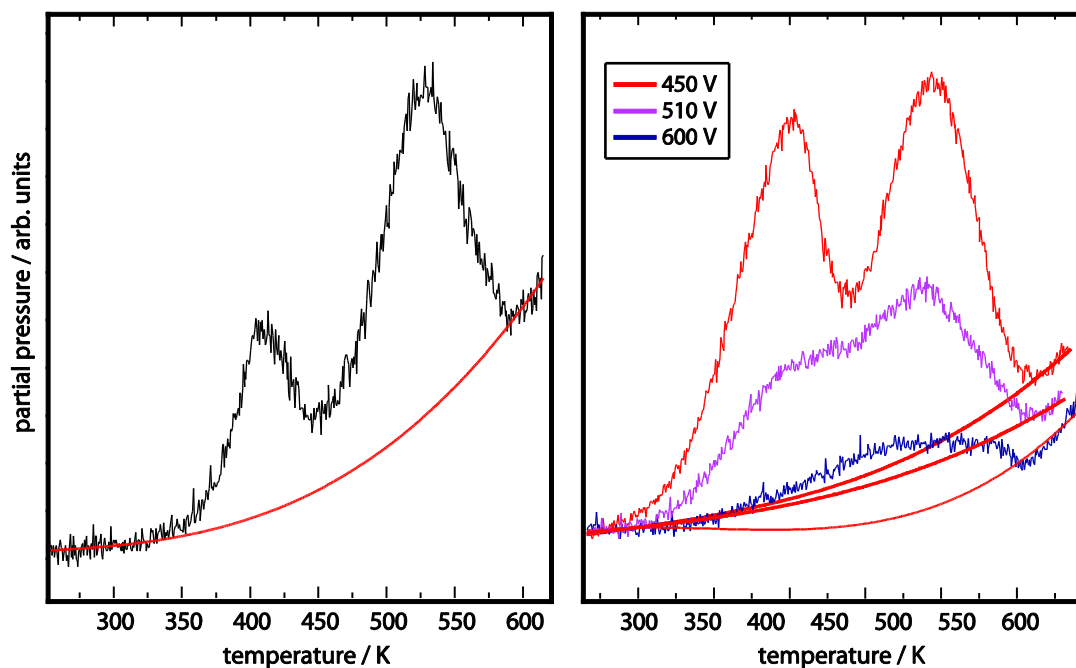
Figure S2: Examples of the baseline correction procedure performed upon all TPD spectra obtained after exposure to activated nitrogen. The first example corresponds to the data shown in Fig. 5(a) of the main paper; the other examples are drawn from Fig. 7. A polynomial of order 3 was fitted to those regions of the spectrum lying outside the temperature range containing the desorption peaks (normally points outside the 350-580 K window). After optimisation of the fit, the polynomial was subtracted from the data to obtain the corrected spectrum.
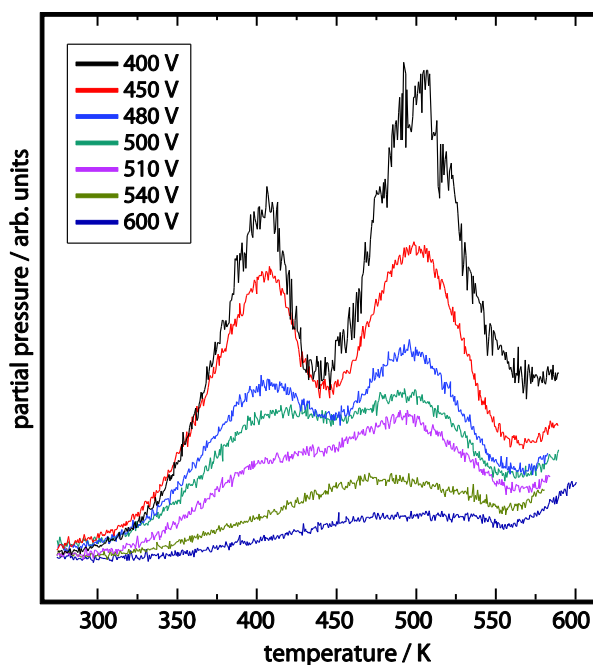

Figure S3: Uncorrected N_2 TPD spectra from $FeS_2\{100\}$, after exposure to activated nitrogen at various nominal ion kinetic energies (Fig. 7 in the text). The N_2^+ ion kinetic energy was reduced from its nominal 500 eV value by applying the indicated positive bias potentials to the sample.
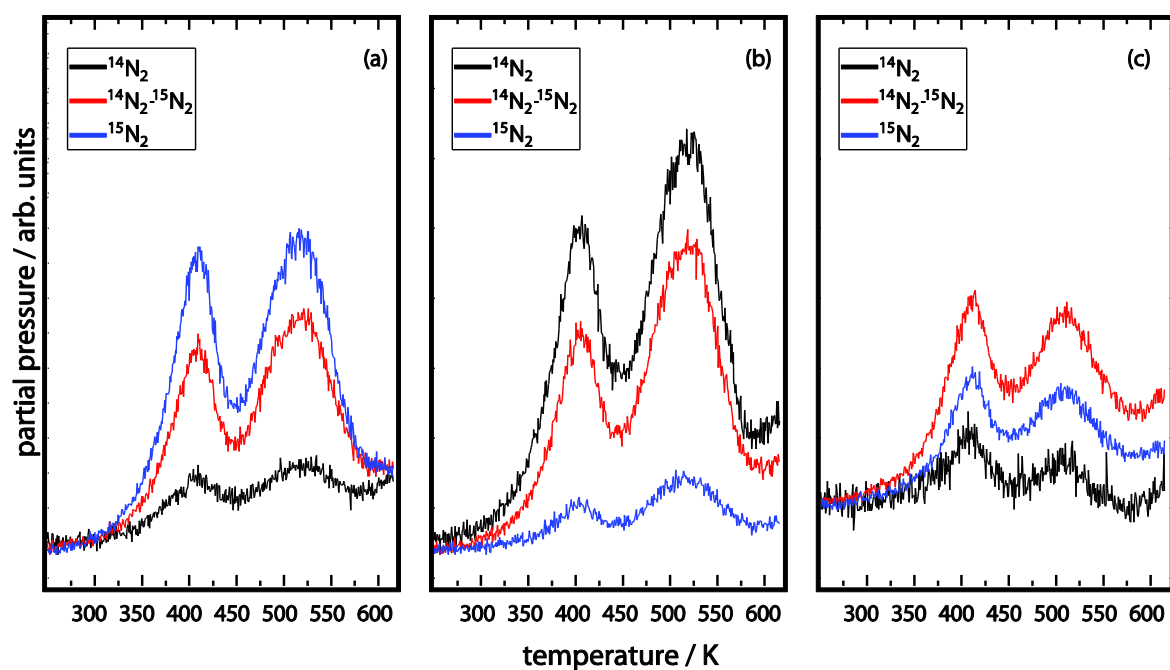
Figure S4: Uncorrected N_2 TPD spectra obtained after exposing $FeS_2\{100\}$ sequentially to equal amounts of activated $^{14}N_2$ and $^{15}N_2$ (Fig. 8 in the text). (a) $^{14}N_2$ followed by $^{15}N_2$, 2 minutes each, +400 V sample bias; (b) $^{15}N_2$ followed by $^{14}N_2$, 2 minutes each, +400 V sample bias; (c) $^{14}N_2$ followed by $^{15}N_2$, 2 minutes each +600 V sample bias.
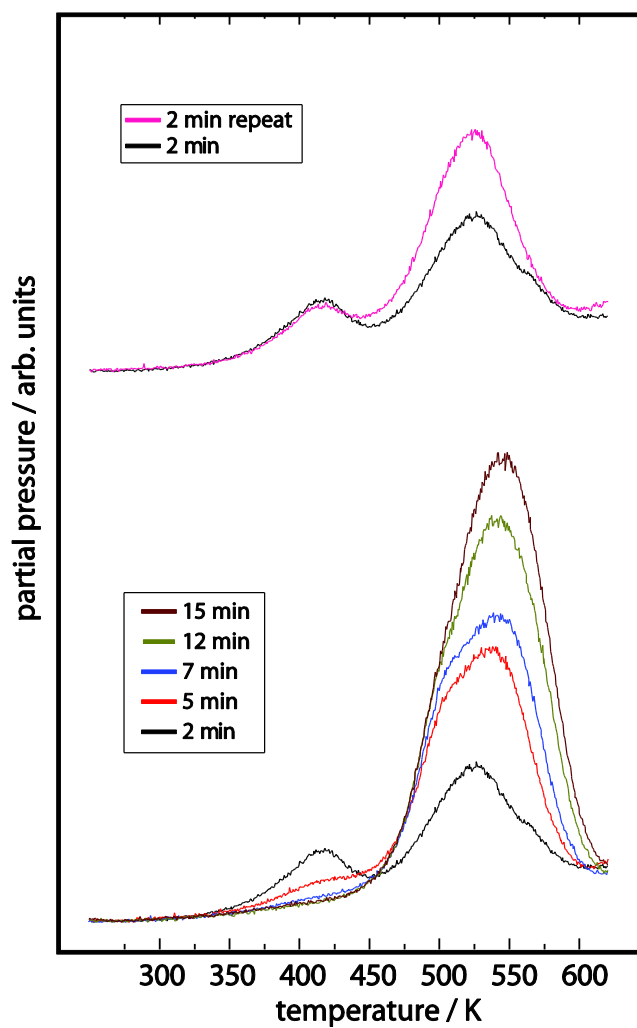
Figure S5: Uncorrected N_2 TPD spectra obtained by subjecting FeS$_2${100} to successively higher exposures to activated nitrogen, including ions at 200 eV nominal kinetic energy (Fig. 9(a) in the text).
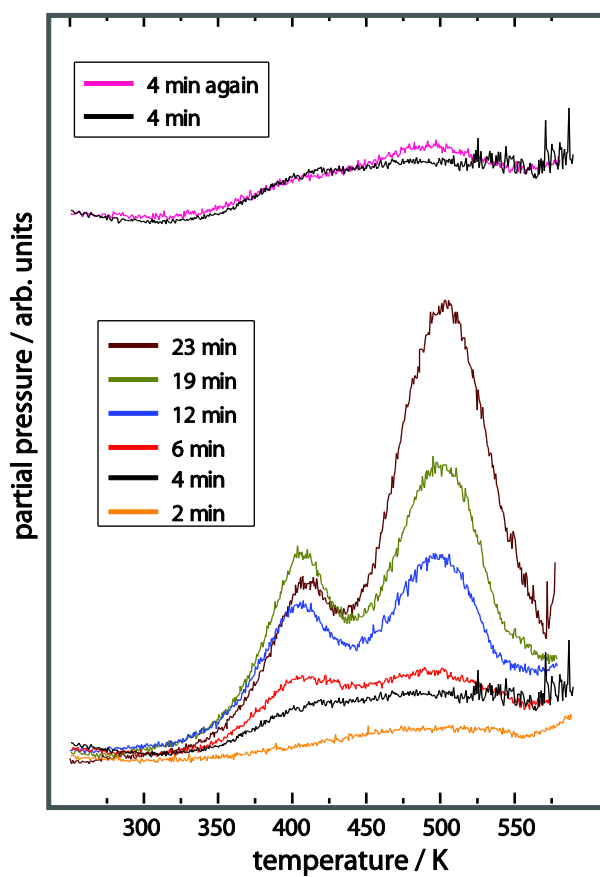
Figure S6: Uncorrected N_2 TPD spectra from $FeS_2\{100\}$ as a function of exposure to activated nitrogen at a sample bias of +600 V (Fig. 10(a) in the text).
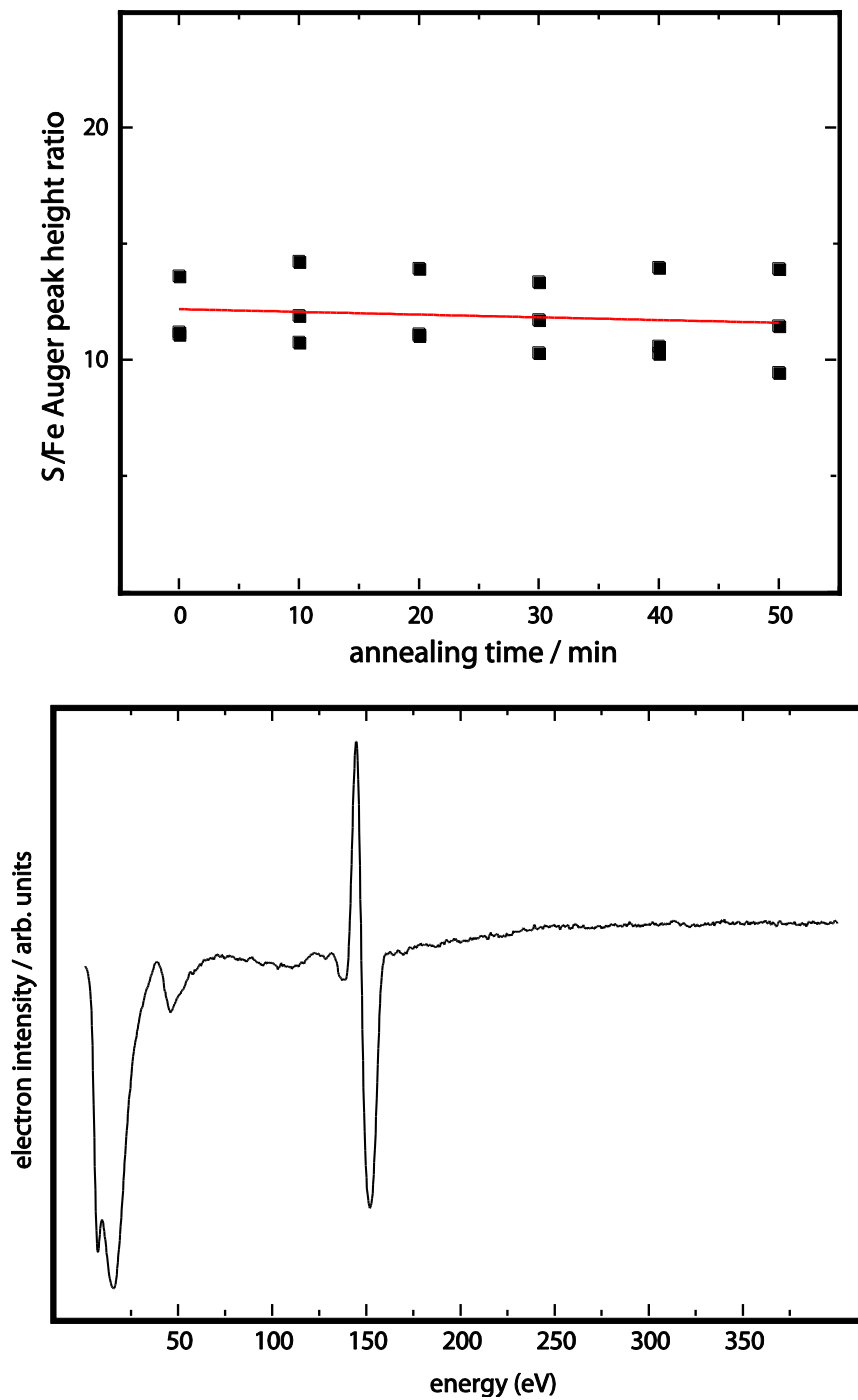
Figure S7: S/Fe Auger peak height ratios obtained through a series of repeated annealing cycles (10 min at 600 K) of an initially stoichiometric surface showing that S/Fe ratio remain constant ($R^2 =$ 0.04). An example of an Auger spectrum, showing the Fe and S peaks at 50 and 150 eV, respectively, used in the analysis, is also shown.
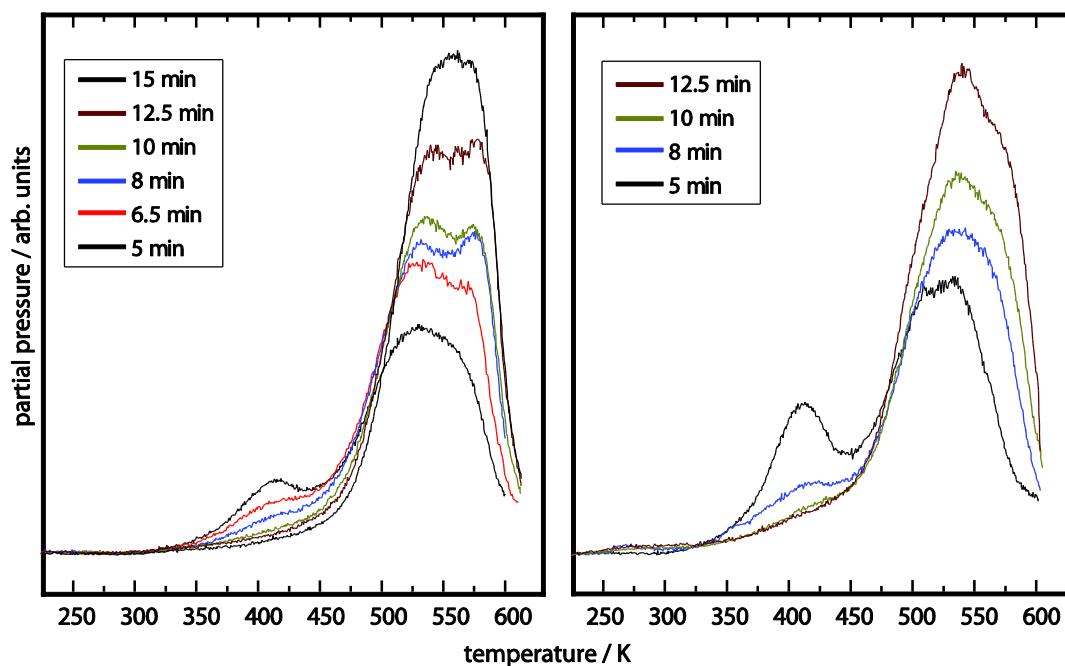
Figure S8: Uncorrected N_2 TPD spectra from $FeS_2\{100\}$ as a function of exposure to activated nitrogen at a sample bias of +350 V (left) and +400 V (right), showing some differences observed in the relative contributions of the two components to the high temperature desorption peak. No systematic trend in these variations was observed, although it is clear that the variability in surface conditions must play a role as it does for the variations regarding the β_1 and β_2 peaks.