In situ TEM and synchrotron SAXS/WAXS study on the impact of different iron salts on iron-catalysed graphitization of cellulose

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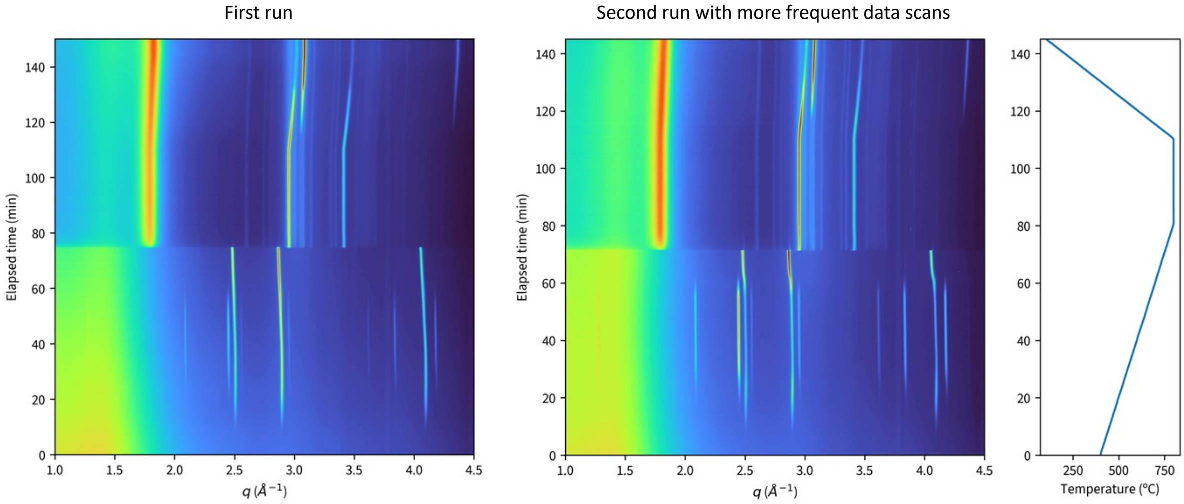
Supplementary Information

1. Supplementary results


First run

Second run with more frequent data scans

Figure S1. *Heatmaps of WAXS data for cellulose-$FeCl_3$ heated to 800 °C, held for 30 minutes and then cooled to room temperature including data for the first run and for a repeated sample with more frequent data scans.*

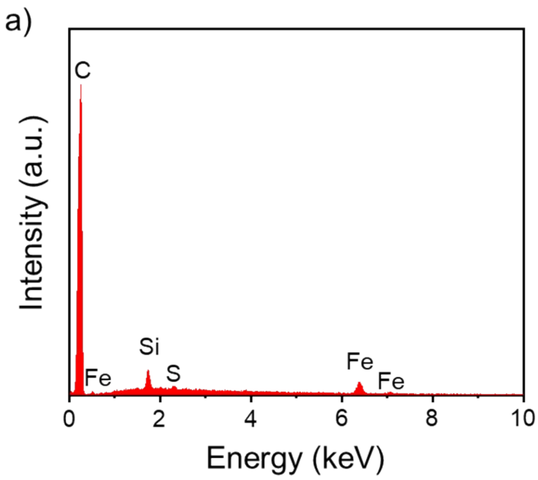


Figure S2. Energy dispersive X-ray analysis (*ex situ*) of a sample of microcrystalline cellulose treated with aqueous $FeCl_3$ and heated to 800 °C for 1 hour under N_2 followed by cooled to room temperature.

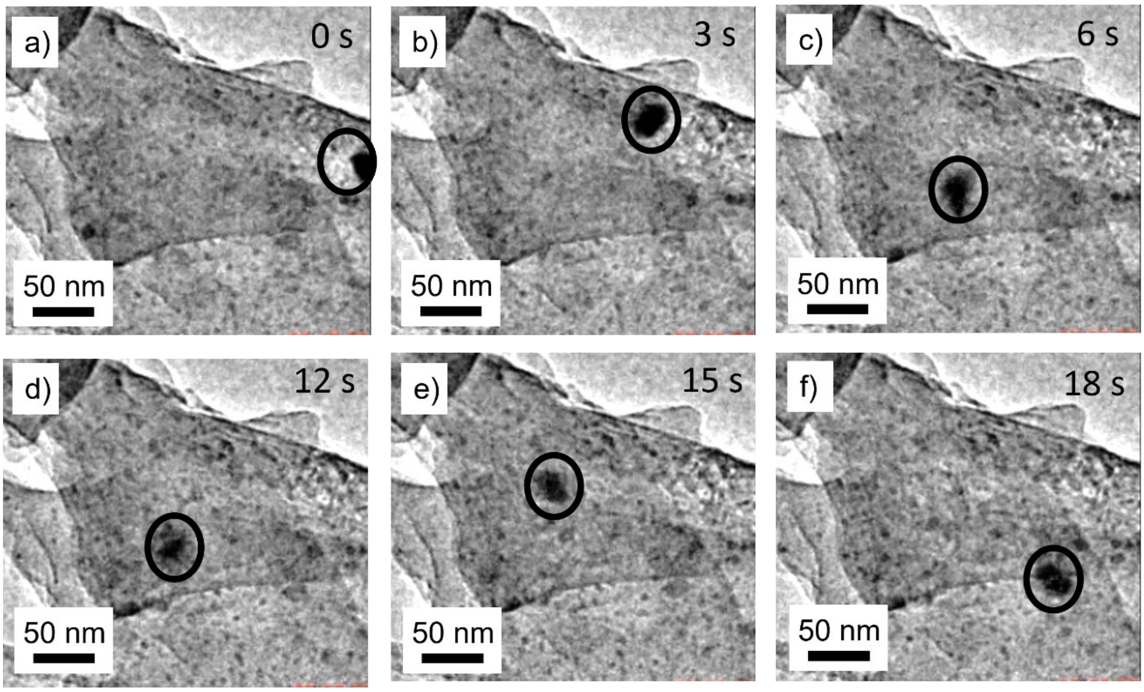


Figure S3. Stills captured from in situ TEM footage of cellulose-$FeCl_3$ derived carbon at 600 °C. The black circle highlights the same particle as it moves through the sample. The speed of the particle is estimated to be 50 nm s^{-1}.

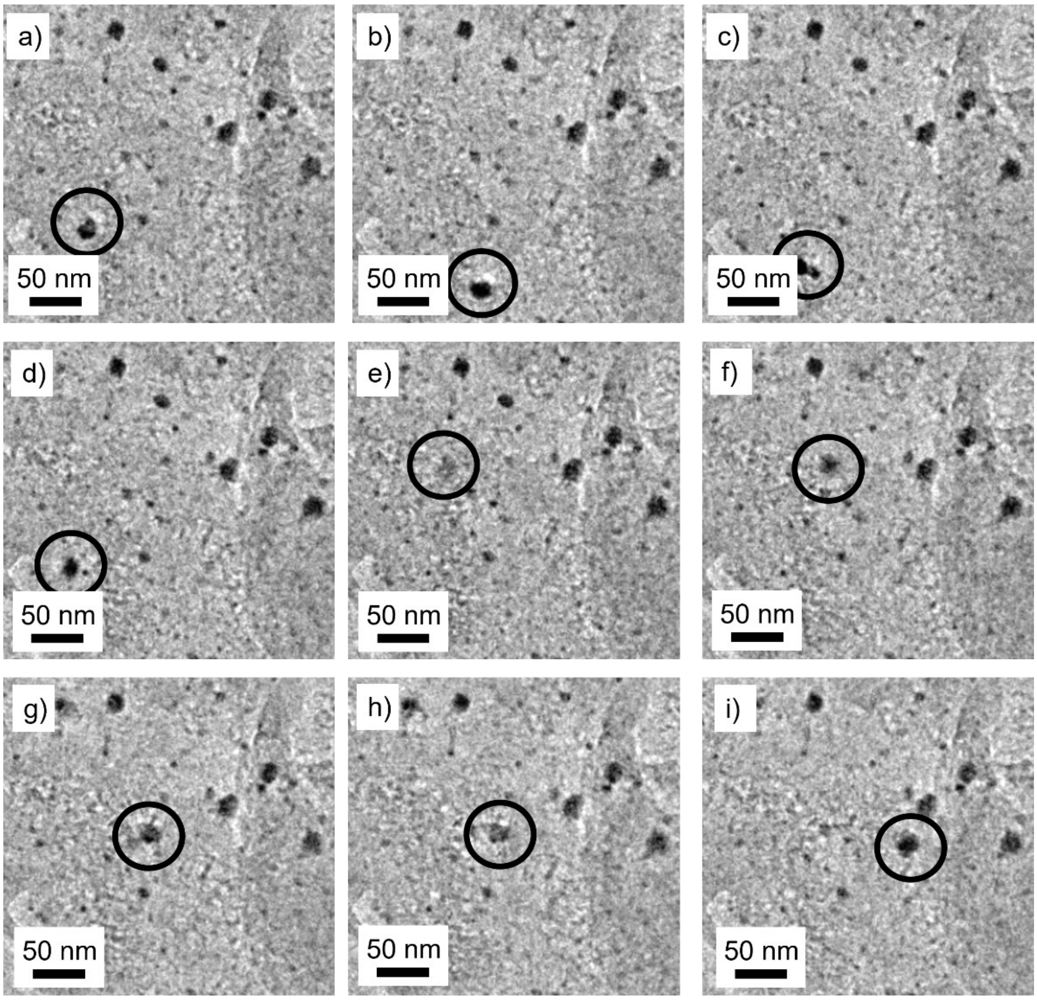


Figure S4. Stills captured from in situ TEM footage of cellulose-$FeCl_3$ derived carbon at 600 °C. The black circle highlights the same particle as it moves through the sample. The speed of the particle is estimated to be 55 nm s^{-1}.

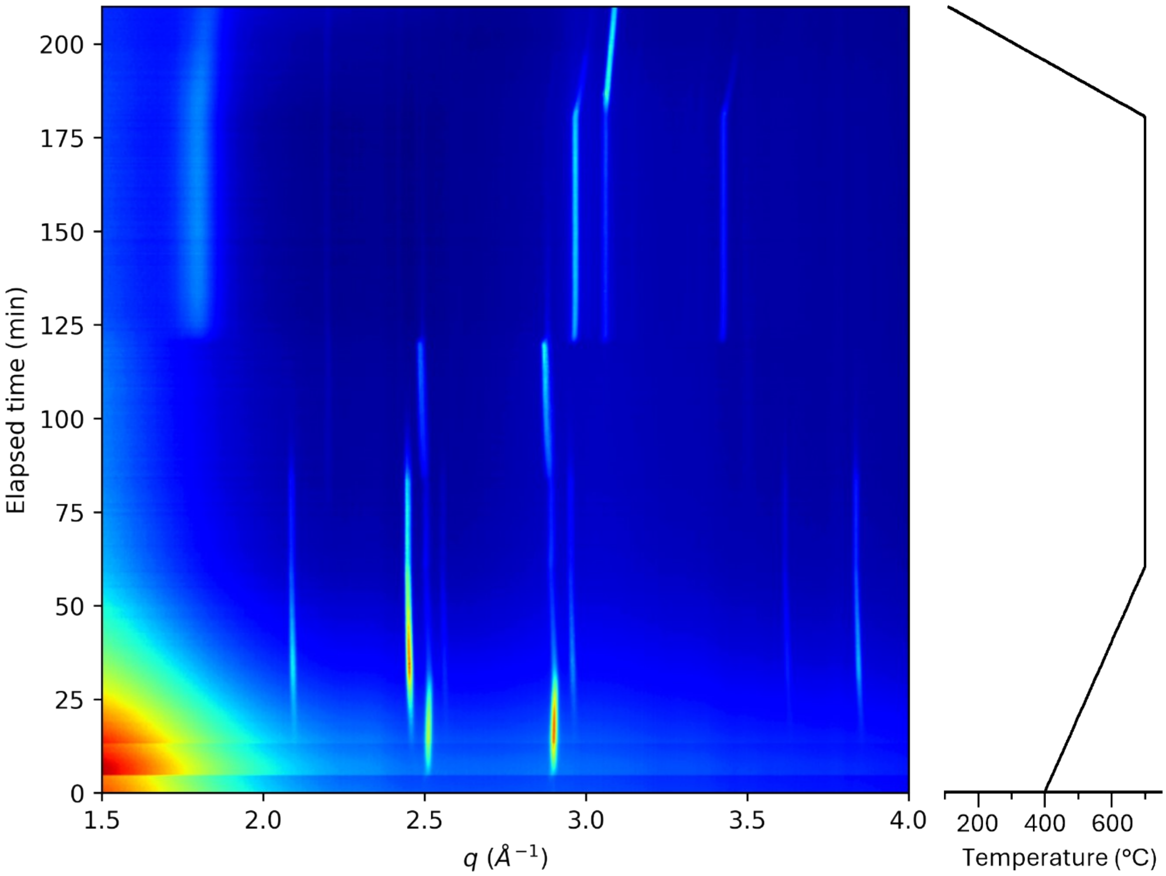


Figure S5. Heatmap of WAXS data for microcrystalline celluose treated with $FeCl_3$ and hested to 700 °C, held for 2 hours and cooled to 100 °C. Additional panel shows the relationship between elapsed time and temperature during the experiment. The figure shows graphitization may occur at 700 °C if held for a longer period of time.

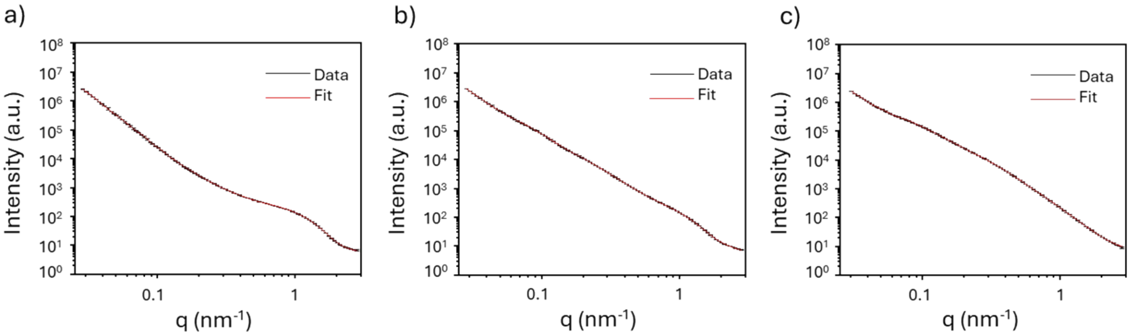


Figure S6. *SAXS data and corresponding fits for cellulose-$Fe(NO_3)_3$ at a) 700 °C, b) 750 °C and c) 800 °C.*

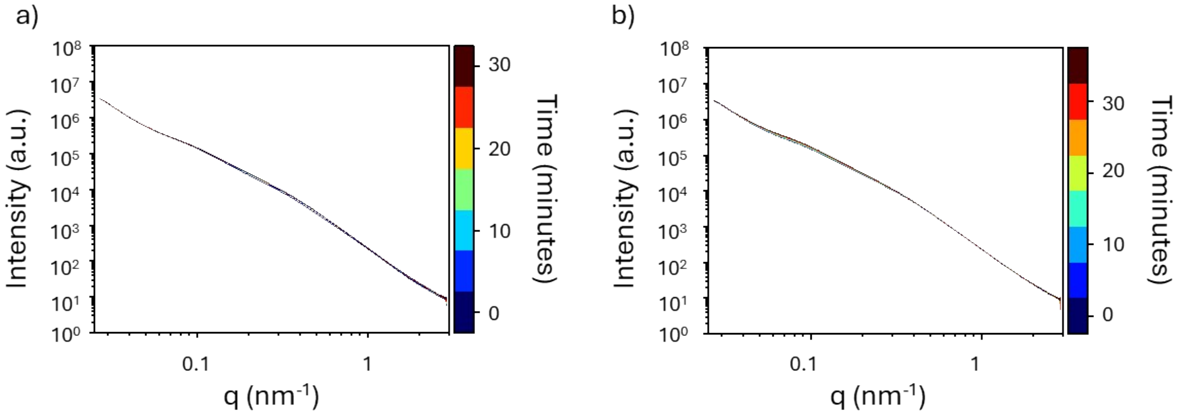


Figure S7. *SAXS data for the a) dwell and b) cooling stages of the cellulose-$Fe(NO_3)_3$ pyrolysis experiment.*

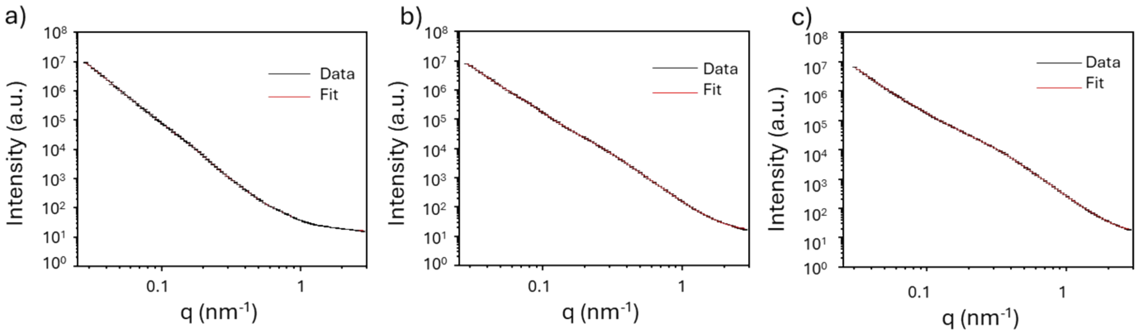


Figure S8. *SAXS data and corresponding fits for cellulose-$FeCl_3$ at 750 °C, 760 °C and 770 °C.*

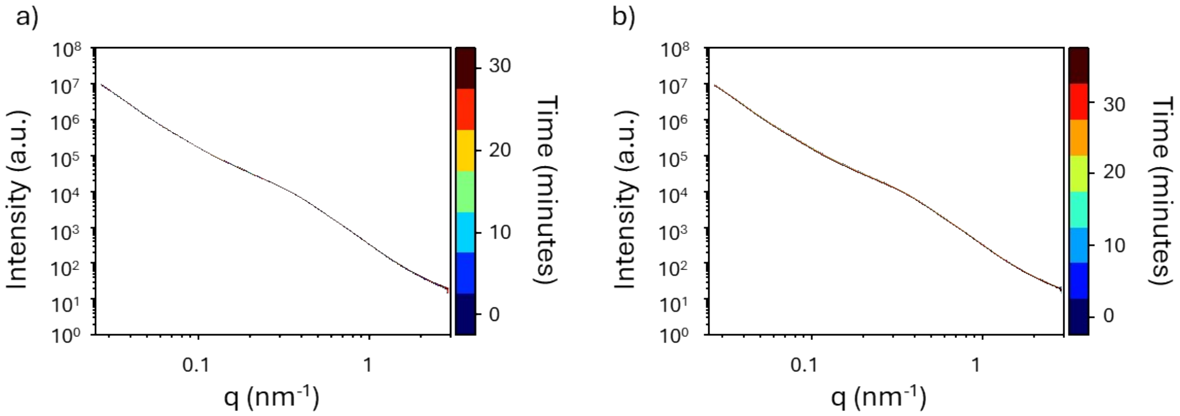


Figure S9. SAXS data for the a) dwell and b) cooling stages of the cellulose-$FeCl_3$ pyrolysis experiment.

2. Supplementary Experimental Information

Experimental Set-up

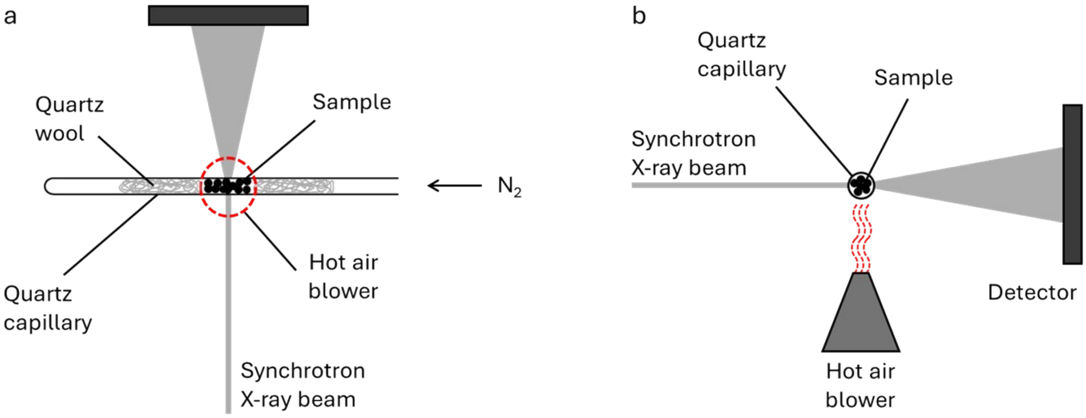


Figure S10. Schematic of the set up for *in situ* SAXS/WAXS experiments.

Rietveld refinements

Phase composition, lattice parameters and crystallite size as a function of temperature for all phases was calculated by Rietveld refinement of synchrotron diffraction data using TOPAS 6 (Bruker AXS, Karlsruhe, Germany). Instrumental broadening was first determined by refining data from a CeO_2 standard using pseudo-Voigt profiles to determine the U, V, W and X parameters describing the angular dependance of peak shapes. The values of these parameters were then fixed for the refinements. Then, *in-situ* measured diffraction data was refined by allowing scale factors, lattice parameters, and crystallite size factors to vary. The (002) reflection from graphitic carbon was described using a split pseudo-Voigt peak. The background was modelled by fitting the scattered intensity at room temperature (where no Bragg reflections were observed) to a series of broad pseudo-Voigt peaks, and their position and intensity was then fixed.

Refinements were performed sequentially, using the refined values obtained from one measurement as the starting point for the following one. Since the samples are essentially amorphous at the beginning of the experiment and the crystalline phases are fully developed by the end, this sequential refinement was performed *in reverse order*, i.e., the last measured diffraction pattern (at room temperature, after cooling) was refined first.

Five crystalline phases were considered for the refinements: Fe_3C (cementite, ICDD #35-0772), α-Fe (ferrite, ICDD #06-0696) and γ-Fe (austenite, ICDD #52-0512) for the samples containing iron nitrate, and additionally FeO (wüstite, ICDD #04-007-8201) and Fe_3O_4 (magnetite, ICDD #00-019-0629) in the chloride samples. Weight fractions of these phases were calculated in the Rietveld method from the refined scale factors and lattice volumes using the well-known formula shown in equation 1.

$$w_p = \frac{s_p(ZMV)_p}{\sum_{i=1}^{n} s_i(ZMV)_i} \times 100\% \qquad \text{Equation 1}$$

Where w_i is the weight fraction in percent and s_i is the scale factor of phase *i,* Z is the number of formula units in the unit cell, M is the mass of the formula unit and V is the unit cell volume. It is important to understand that while the scale factor is proportional to the amount of each phase present in the sample, the weight fraction is normalized so that it sums to 100%. This means that during the early stages of graphitization and Fe/Fe_3C crystallization, the values for the scale factors are relatively low and therefore the weight fractions have large uncertainties. Furthermore, since we cannot describe the background from amorphous carbon as a crystalline phase, we cannot normalize to all phases in the sample.