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Supporting Information

Unravelling the Growth Mechanism of the Co-Precipitation of Iron Oxide Nanoparticles with the Aid of Synchrotron X-Ray Diffraction in Solution

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1. Estimation of Mixing Time

The Villermaux-Dushman protocol was used to estimate the (micro) mixing time achieved in the used T-mixer following the procedures for experimental characterisation of micromixers described by Commenge and Falk[1] using the concentrations for the H_2SO_4 solution and the iodide/iodate buffer solution denoted by the authors as 1 and 1c in table 1 of their work. The different acid and buffer concentration were needed to achieve the highest accuracy for the different mixing times which decreases with increasing flow rates. The mixing time was obtained from the triiodide absorption at 353 nm (using the same equipment described in the previous section) and equation 17 in the work of Commenge and Falk.[1] This empirical equation relates the triiodide absorption and the concentrations of the H_2SO_4 and iodide/iodate buffer solution to mixing times computed *via* an interaction by exchange with the mean (IEM) model. Further information on the IEM mixing model was described by Falk and Commenge.[2] To the best of our knowledge, there are no studies using the Villermaux-Dushman protocol at temperatures other than room temperature (the reaction kinetics of the competitive reactions and equilibrium of triiodide will change). Therefore, the mixing time in the T-mixer at 60°C could not be obtained directly, which is why the Reynolds number (Re) was used to estimate the corresponding mixing time at the reaction temperature.

At the used reaction temperature of 60 °C, the viscosity of water drops significantly, which is expected to yield faster mixing for the same flow rates. At 60 °C and a flow rate of 10 ml min^{-1} (= 2 × 5 ml min^{-1}), the Re number in the outlet channel of the T-mixer is ~900. At room temperature, this Re number would be obtained in the T-mixer for flow rates of 21 ml min^{-1}. For the latter flow rate, the mixing time was determined to be 30 ms *via* the Villermaux-Dushman protocol at room temperature. It should be noted that techniques such as the Villermaux-Dushman protocol, cannot be expected to provide accurate mixing time quantifications, rather than an order of magnitude estimation. Hence, the mixing time during the synthesis was estimated to be < 50 ms.

2. Synchrotron X-Ray Diffraction

The raw radially averaged data for the synchrotron X-ray diffraction (XRD) are shown in Fig. S1 before background subtraction and conversion to a calculated 2theta value based on the wavelength of Cu Kα. The patterns were taken with an X-ray wavelength of 1 Å. The background that was subtracted from the data sets is in blue as the blank sample and was taken with the sodium carbonate solution in the capillary (Fig. S1). The background subtraction was carried out by subtracting the blank measurement from the later measurements.
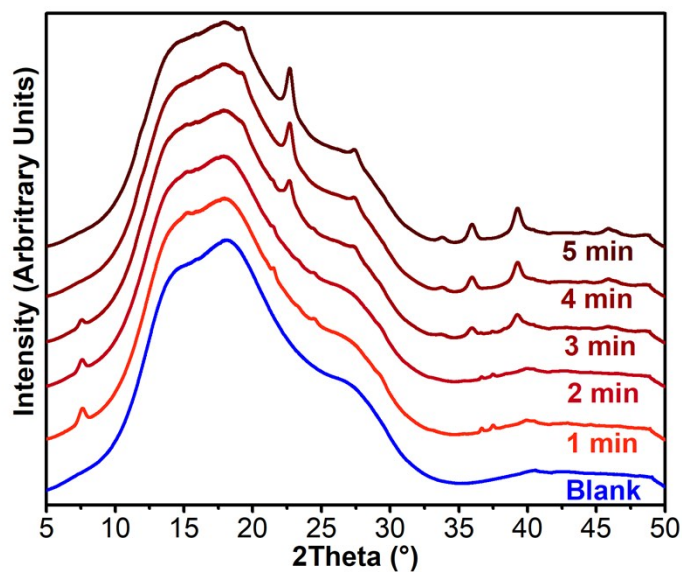

Fig. S1 Radially averaged synchrotron XRD patterns as taken for the blank, 1, 2, 3, 4, and 5 min samples.

The background subtracted data with the original 2theta value is shown in Fig. S1, with the reference patterns of maghemite, magnetite and iron hydroxide carbonate.
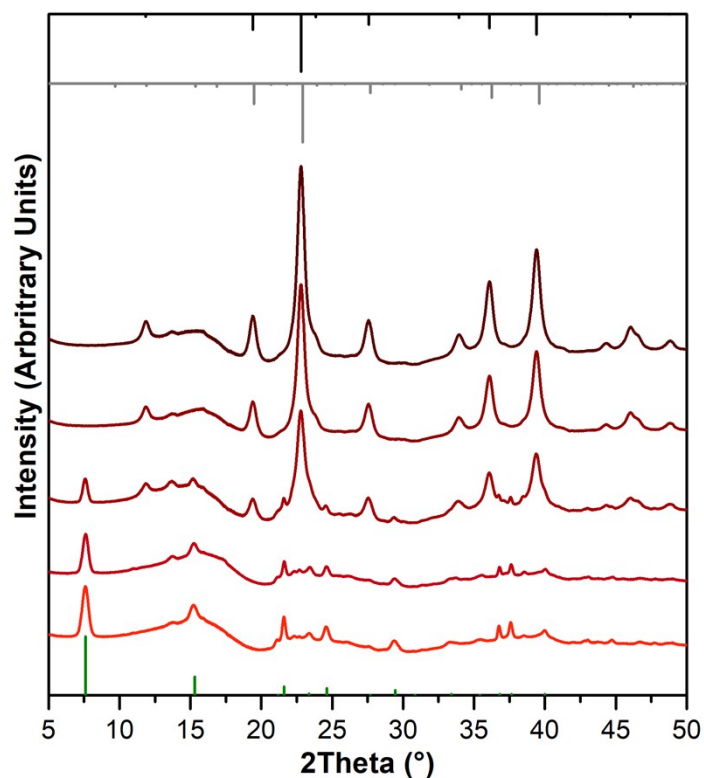
Fig. S2 Background subtracted synchrotron X-ray diffraction with an X-ray wavelength of 1 Å, with the iron hydroxide carbonate reference pattern (PDF ref. 00-046-0098) shown in green, maghemite reference pattern (PDF ref. 00-039-1346) at the top in grey and magnetite reference pattern (PDF ref. 03-065-3107) at the top in black.

Upon injecting the reaction mixture into the capillary no additional phase changes were observed over an additional 9 min of observation (Fig. S3). The only changes observed was a slight drop in intensity of the signal as settling occurred.
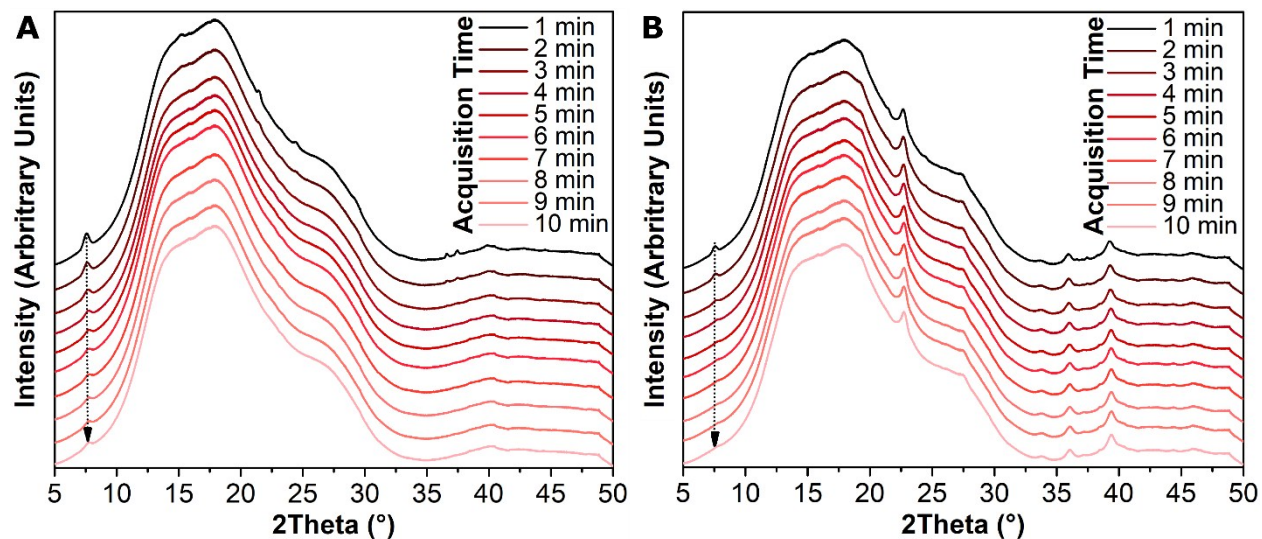

Fig. S3 Radially averaged synchrotron X-ray diffraction patterns taken every minute until 10 min after the acquisition was started with an X-ray wavelength of 1 Å for both the reaction after (A) 1 min and (B) 3 min. The data is without background subtraction.

3. Ultra Violet – Visible Spectroscopy

Ultra Violet – Visible Spectroscopy (UV-Vis) absorption spectra of the solution at 1, 2, 3, 4, and 5 min were recorded *via* an USB 2000+ Spectrometer and a DT-Mini-2-GS light source (Ocean Optics Inc., USA). A 200 µL aliquot of the sample was diluted 200 times in a sodium carbonate solution of pH 9 (*i.e.,* the final pH value of the nanoparticle solution as synthesised). Subsequently, the diluted sample was poured into a plastic cuvette and measured. The results shown in Fig. S4, indicate temporal change of the UV-Vis spectra that is of the same time-scale as the structural changes observed *via* XRD and TEM studies. The increase in absorbance during the first 3 min (while the shape of the spectra changes only marginally) indicates the formation of the initial phases during that time interval. Subsequently, the spectral shape changes quickly during the next 2 min (min 4-5) and remains constant afterwards (measurement after 10 min not shown here).
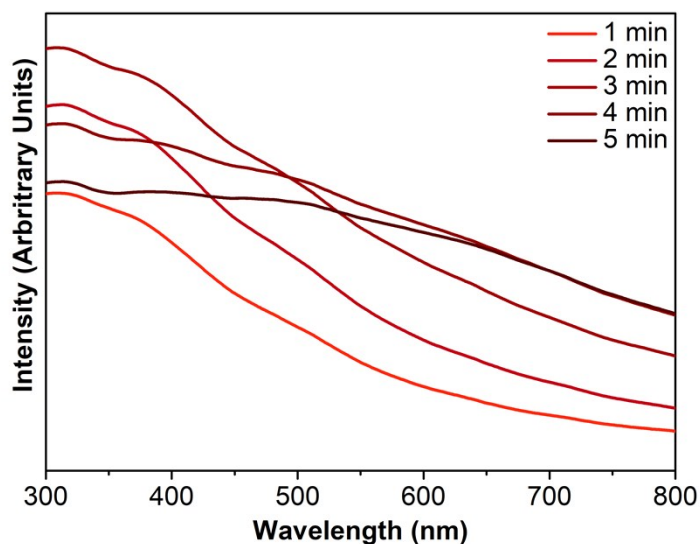

Fig. S4 UV-Vis spectra taken from the samples diluted 200 times in pH 9 solution after 1, 2, 3, 4, and 5 min of reaction.

4. Electron Diffraction

The electron diffraction patterns (Fig. S5) were all obtained and calibrated with a gold calibration sample. The patterns were radially averaged and normalised and presented in Fig. 2D of the main text.
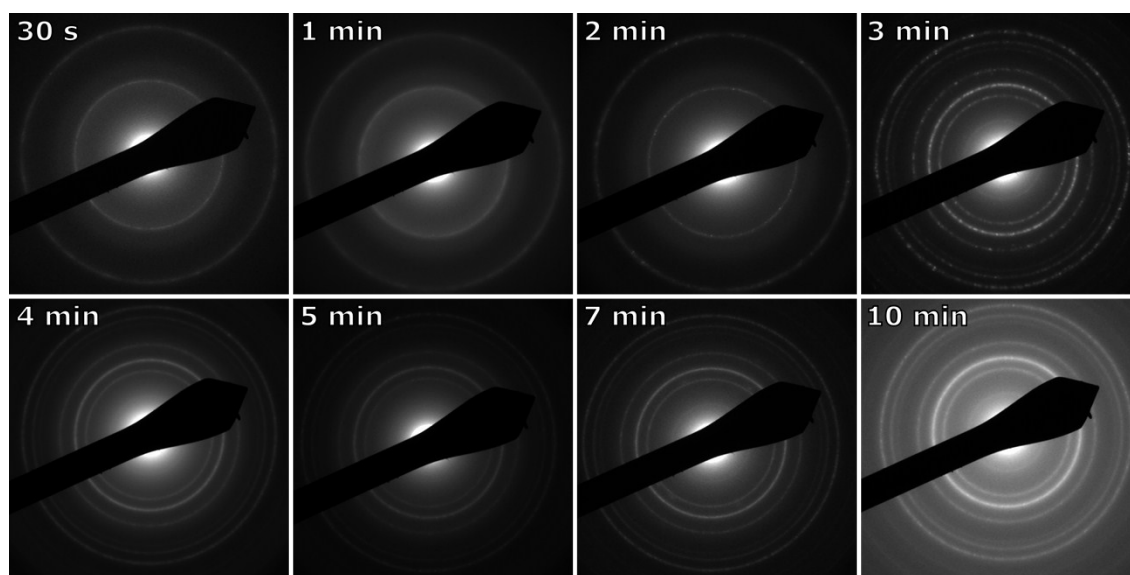

Fig. S5 Electron diffraction patterns of the samples after 30 s, 1, 2, 3, 4, 5, 7 and 10 min.

5. Reactions with Fe^{2+} and Fe^{3+} only

Control experiments were carried out under the same conditions as shown in the main text, except with 0.1 M of only $FeCl_2$ 4H_2O (Fig. S6A) or $FeCl_3$ 6H_2O (Fig. S6B). The results showed large plates with $FeCl_2$ 4H_2O only (Fig. S6A), and small spherical particles for $FeCl_3$ 6H_2O only (Fig. S6B), similar to both precipitates observed in the main text. The plates formed from $FeCl_2$ 4H_2O showing the same electron diffraction peaks (Fig. S6C) as reported for the samples in Fig. 2D, and the electron diffraction from the particles formed with $FeCl_3$ 6H_2O showing very broad rings (Fig. S6D).
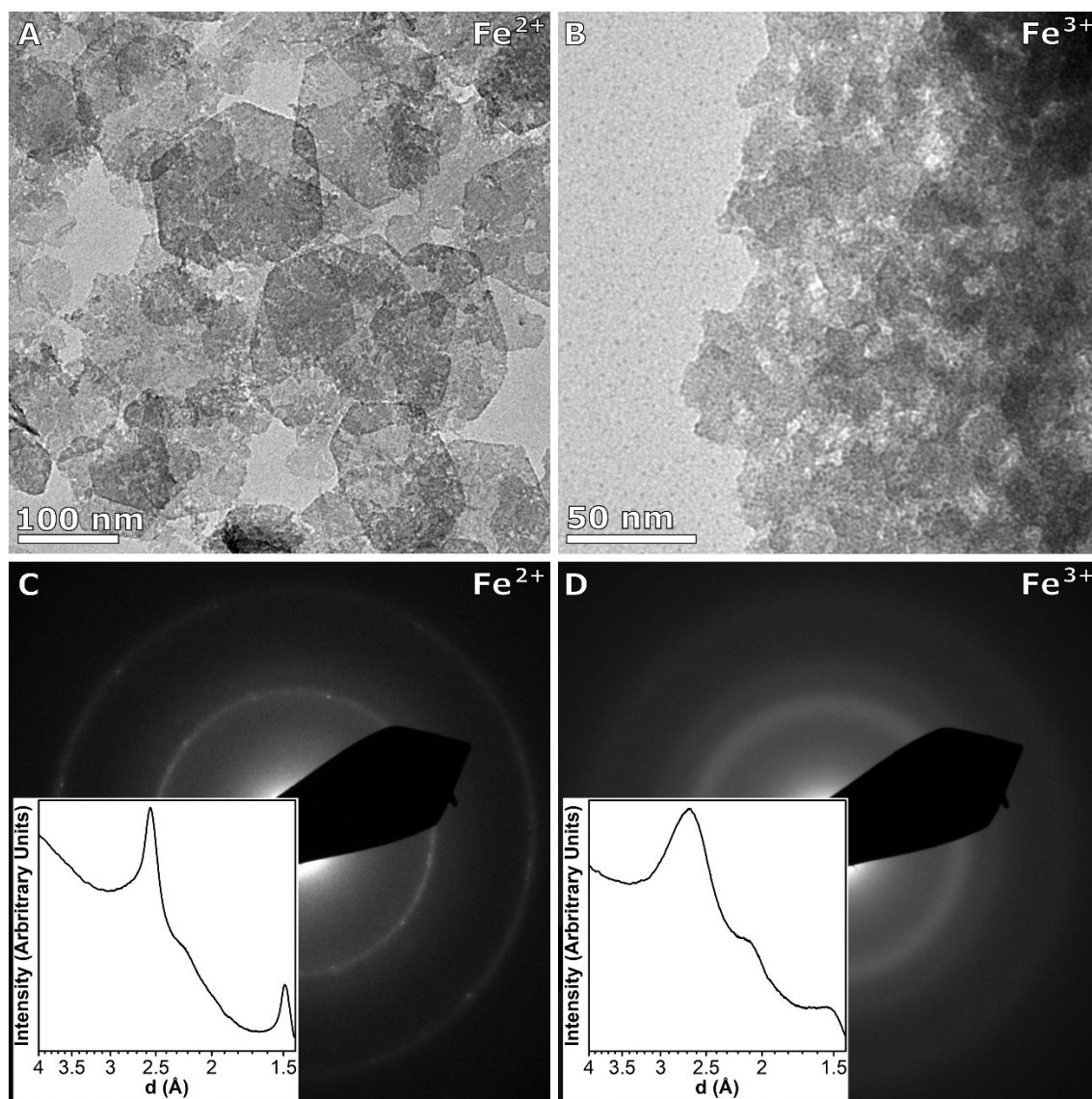

Fig. S6 TEM images of particles formed after 2 min of reaction with only (A) $FeCl_2$ 4H_2O or B) $FeCl_3$ 6H_2O as the precursor. (C) and (D) are the electron diffraction patterns of (A) and (B) respectively, with the radially averaged data as the insets.

6. Room temperature ^{57}Fe Mössbauer Spectroscopy

To compare with the Room temperature ^{57}Fe Mössbauer spectroscopy for the 1 min sample, measurements were also carried out on the sample prepared with Fe^{3+} only (Fig. S7). The sample showed similar results to the 1 min sample, showing that the ferrihydrite was being formed from the Fe^{3+} precursor in solution.
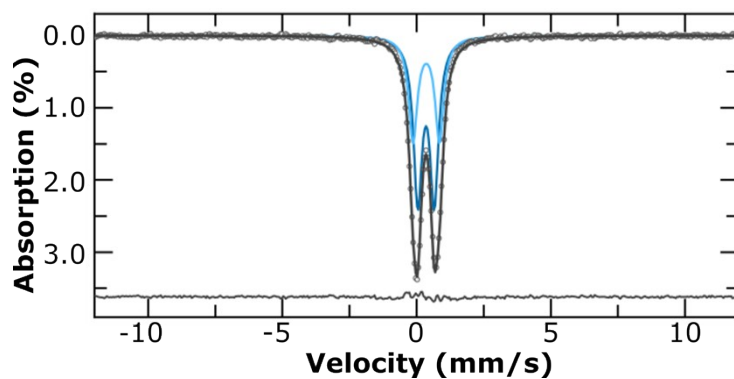

Fig. S7 Room temperature ^{57}Fe Mössbauer Spectroscopy results from the 1 min reaction of Fe^{3+} only with fitting of the different components included.

7. References

1. J.-M. Commenge and L. Falk, Villermaux–Dushman protocol for experimental characterization of micromixers. *Chem. Eng. Process.* 2011, **50**, 979.

2. L. Falk and J.-M. Commenge, Performance comparison of micromixers. *Chem. Eng. Sci.* 2010, **65**, 405.