Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Scalable synthesis of dispersible iron carbide (Fe_3C) nanoparticles by 'nanocasting': Supplementary Information

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1. Experimental Details

1.1 Synthesis of MgO/Fe_3C composites

Prussian blue nanoparticles were prepared by dissolving $FeCl_2.4H_2O$ (0.6 g) and polyvinylpyrollidone (1:1 molar ratio) in deionised water (240 ml). Separately, $K_3[Fe(CN)_6]$ (0.99 g) was dissolved in deionised water (60 ml) and the resulting solution added dropwise to the $FeCl_2$ solution with vigorous stirring. The solution was stirred for a further 30 minutes then acetone (300 ml) added to induce agglomeration of the Prussian blue particles. The particles were washed three times with acetone via centrifugation and the dark blue solid transferred into methanol (300 ml). MgO nanopowder (Sigma Aldrich 549649 <50 nm) was added to give a 1:1 mass ratio of Prussian blue to MgO and the mixture stirred thoroughly before removing the methanol by rotary evaporation. The pale blue solid was further dried at 70 °C in air for 24 hours. To prepare MgO/Fe_3C nanoparticle composites, the Prussian blue/MgO mixture was heated at 5 °C/min to 800 °C under N_2 in a tube furnace with 1 hour hold.

The large scale synthesis of Fe_3C nanoparticles was carried out by mixing commercial soluble Prussian blue (Sigma Aldrich 03899) with MgO nanopowder (Sigma Aldrich 549649) in a pestle and mortar. The pale blue mixture was transferred to a crucible and heated at 5 °C/min to 800 °C under N_2 in a tube furnace with 1 hour hold.

1.2 Washing MgO/Fe_3C samples with ethylenediamine tetraacetic acid (EDTA)

To isolate dispersible Fe_3C nanoparticles, the MgO was removed from MgO/Fe_3C samples by washing with aqueous EDTA. In this paper, the MgO/Fe_3C solid was treated by stirring overnight in 0.2 M aqueous EDTA (7% molar excess relative to MgO content) followed by washing the sample three times with deionised water and ethanol using centrifugation. The resulting solid was dried in air for 24 hours at room temperature. Atomic absorption spectroscopy of the supernatant solution from the final water wash showed a Mg content of 2% (by mass). A higher concentration of EDTA can be used to reduce this to <0.1% but this was observed by X-ray diffraction to dissolve a significant amount of Fe_3C. Aqueous HCl should not be used to remove MgO in this system as it either produces $Mg(OH)_2$ or, if more concentrated, results in Fe_3C dissolution.

1.3 Hydrogen peroxide to remove amorphous carbon

0.2 g of Fe_3C/C sample was added to hydrogen peroxide (H_2O_2) solution (20 ml) and the mixture stirred for 2 hours. The hydrogen peroxide concentrations used were 0%, 0.1%, 1%, 5% and 10%. The resulting suspensions were separated by centrifuging for 5 minutes at 10000 rpm and the supernatant decanted for analysis. The solid samples were washed with water then dried overnight under vacuum at 70 °C.

1.4 Preparation of a ferrofluid

For preparation of a ferrofluid, commercial soluble Prussian blue (($KFe^{III}[Fe^{II}(CN)_6]$, 7.5 g, Sigma Aldrich 03899) was ground in a pestle and mortar with commercial MgO nanopowder (Sigma Aldrich 549649 <50 nm, 7.5 g). Note that 'soluble' Prussian blue is not truly soluble but is in a nanoparticle form that can be used to prepare colloidal suspensions in water. The resulting pale blue powder was pyrolyzed and washed with EDTA as above. A ferrofluid was prepared by sonicating the resulting Fe_3C nanoparticle powder (0.1 g) in DI water (5 ml) and oleic acid (0.16 ml) for 1 hour. The black powder collected as a suspension in the oleic acid layer, which was separated from the water layer using a $SmCo_{26}$ magnet. The black fluid was washed three times with ethanol and then three times with kerosene, collecting each time using magnetic separation.

1.5 Dispersion of Fe_3C nanoparticles on a support

For dispersion of particles on a silica support, a Fe_3C/MgO mixture was prepared from as-synthesized Prussian blue with MgO nanopowder then washed with EDTA and H_2O_2 as described above. 3 mg of the resulting black powder was dispersed by sonication for 30 minutes in 300 µl deionised water with Cetyltrimethylammonium bromide (CTAB) surfactant (0.03 mg). The resulting solution was sonicated for 30 minutes with 0.1 g silica (a standard support material kindly provided by Johnson-Matthey) then dried at room temperature for 24 hours.

1.6 SAXS/WAXS

SAXS/WAXS measurements were done using the Multiscale Analyser for Ultrafine Structures (MAUS): a heavily customized Xeuss 2.0 (Xenocs, France), installed at the Bundesanstalt für Materialforschung und -prüfung, Berlin. The MAUS uses X-rays from microfocus X-ray tubes, followed by a multilayer optics to parallelize and monochromatize the X-ray beams to a wavelength of λ_{Cu}=0.154 nm for the copper source, and λ_{Mo}=0.071 nm for the molybdenum source. These are collimated using three sets of scatterless slits (two germanium and one silicon, with the latter virtually transparent to molybdenum radiation, but very effective for the copper radiation). The detector is an in-vacuum Dectris Eiger R 1M on a motorized platform, for this investigation placed at distances of ranging from 70 - 2500 mm from the sample (after correction, the data from the different distances and different sources overlap to form a single curve). The sample-to-detector distance is traceably calibrated using a triangulation method, double-checked with interferometer strip readings. The space between the start of the collimation until the detector is a continuous, uninterrupted vacuum to reduce background. The powders were mounted in a flat sample holder, between two pieces of scotch magic tape. By using both photon energies over a range of overlapping sample-to-detector distances, a very wide range in scattering angles is covered, and the low (but measurable) fluorescence from the iron-containing samples is avoided. The resulting data has been processed using the DAWN software package,[1,2] with the following processing steps in order: masking, correction for counting time, dark-current, transmission, primary beam flux, background (no sample in the beam), detector efficiency, flat-field, and solid angle, followed by a thickness correction and azimuthal averaging. The apparent sample thickness was estimated by using the sample absorption, composition and gravimetric density, allowing the data to be scaled to absolute units in combination with the flux and transmission corrections using the full beam on the

Eiger detector. Scaling of the individual datasets from the various distances and sources to achieve overlap was, by virtue of these corrections, rendered unnecessary. Photon counting uncertainties were propagated through the correction steps.

1.7 Other instrumentation

X-ray diffraction was carried out on a Panalytical Empyrean with a Copper X-ray source. HAADF images, EDS mapping and electron tomography was carried out on an FEI Talos F200X Scanning Transmission Electron Microscope. Other TEM images were acquired on a JEOL 2100F TEM.

2. Supplementary Results and Discussion

2.1 Control sample

A TEM image of a sample of Fe_3C (confirmed by XRD – not shown) produced by heating Prussian Blue without an MgO cast) is shown in Figure S1.

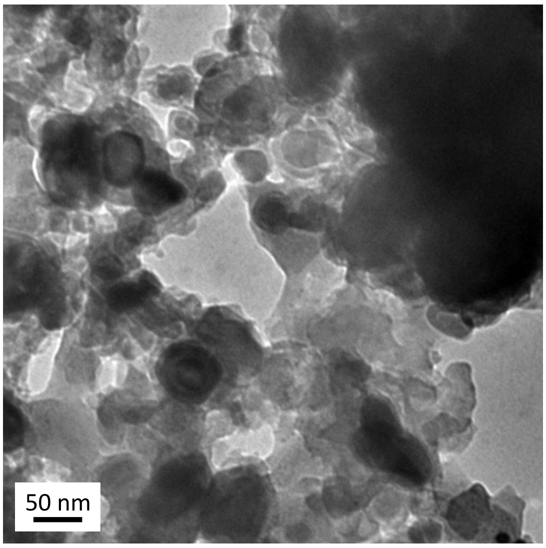

Figure S1 *TEM image of a control sample of Prussian Blue heated to 800 °C without MgO.*

2.2 Removal of excess carbon from the sample using hydrogen peroxide (H_2O_2)

X-ray diffraction patterns of samples before and after washing with various concentrations of H_2O_2 are shown in Figure S1. The absence of peaks for iron oxide phases, and the presence of the iron carbide peaks in all samples suggests that the Fe_3C is protected from the H_2O_2 by the graphitic carbon shells. Atomic adsorption spectroscopy was used to probe the iron content of the H_2O_2 solutions after they had been used to wash the Fe_3C/C samples. For every concentration of H_2O_2, the content of the supernatant solution was <1 ppm, confirming that the Fe_3C nanoparticles are protected from oxidation.

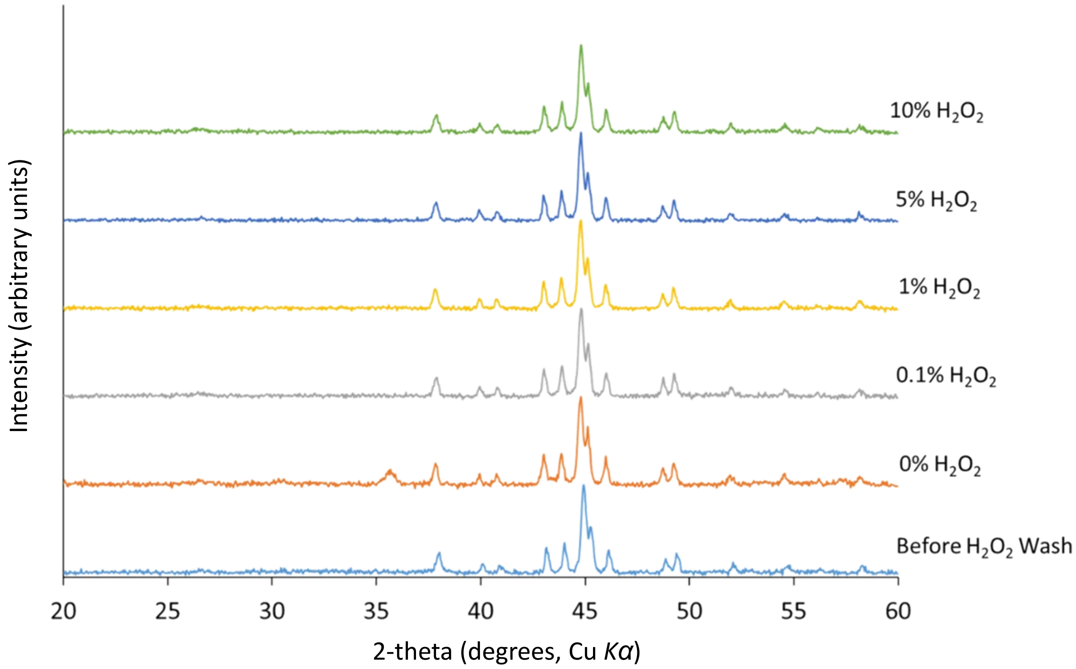

Figure S2 *X-ray diffraction patterns of Fe_3C sample after washing with H_2O_2 at various concentrations, showing that the hydrogen peroxide does not appear to affect the iron carbide in the sample.*

2.3 Supplementary SQUID data

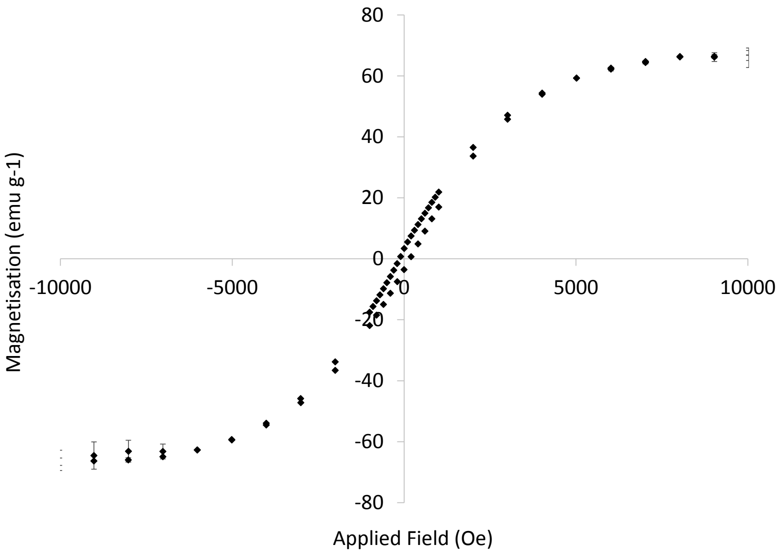

Figure S3 *Plot of the field dependence of the isothermal magnetization at 300 K for a sample of MgO-cast Fe_3C nanopowder.*

2.4 SAXS/WAXS analysis

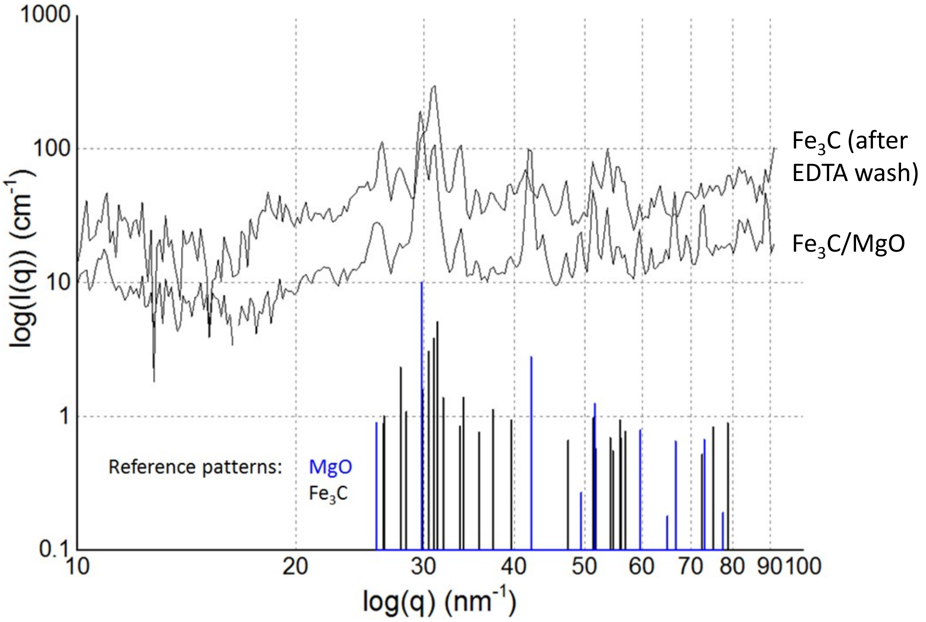

Figure S4 Wide-angle X-ray scattering data for samples of Fe_3C/MgO and Fe_3C, with the corresponding reference patterns.

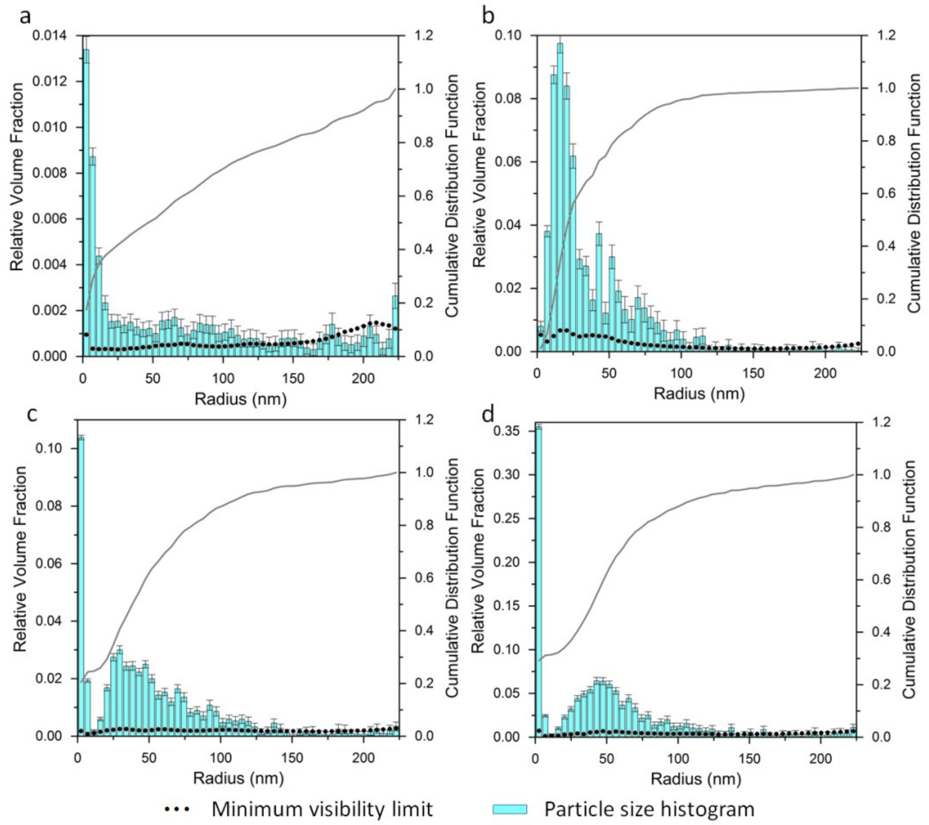

Figure S5 Particle size histograms coupled with visibility limits (black dots, left y-axis) and cumulative distribution functions (right y-axis) plotted on a linear x-axis for a) Prussian Blue/MgO, b) Fe_3C/MgO, c) Fe_3C (after EDTA treatment) and d) Fe_3C (after EDTA then H_2O_2 treatment).

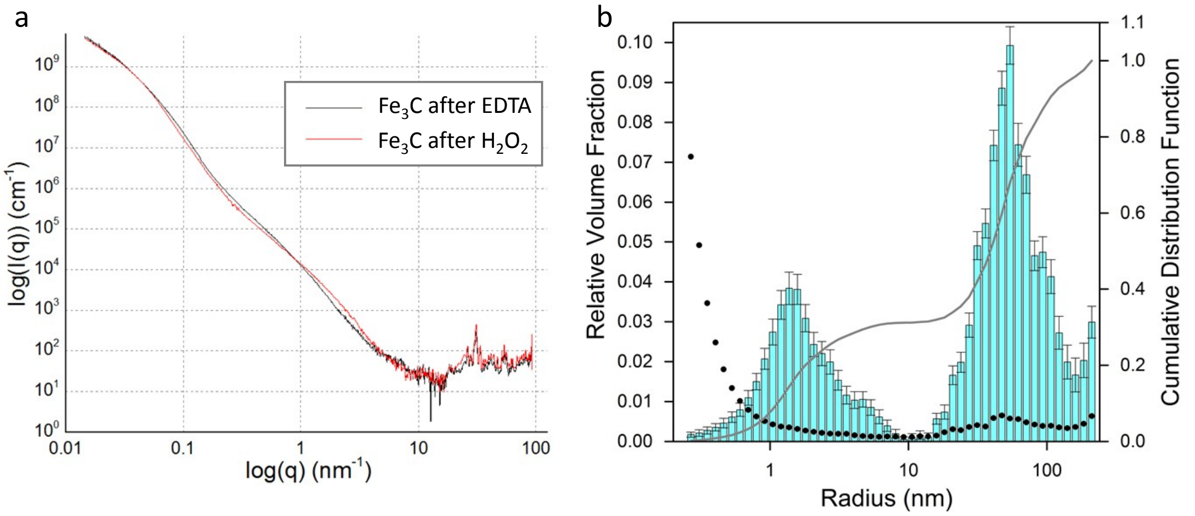

Figure S6 (a) SAXS and WAXS data fit for Fe_3C nanoparticles after EDTA and H_2O_2 treatment and (b) size distribution data for the sample after H_2O_2 treatment.

2.5 Scaled-up synthesis for preparation of a ferrofluid

Large samples of dispersible Fe_3C nanoparticles were prepared as described in the experimental section of the main paper by grinding commercial soluble Prussian blue powder with commercial MgO nanopowder. TEM images (below) confirmed that the resulting Fe_3C material is still nanoparticulate.

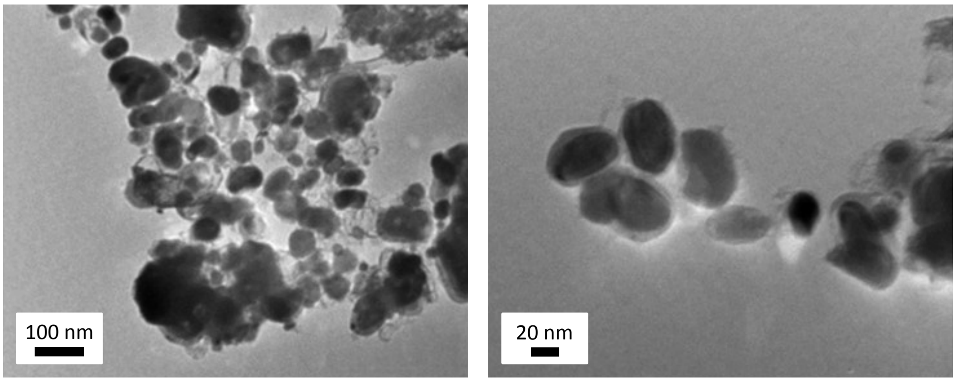

Figure S7 *TEM images of Fe_3C powder prepared by a scaled-up synthesis, showing that nanoparticles are still formed.*

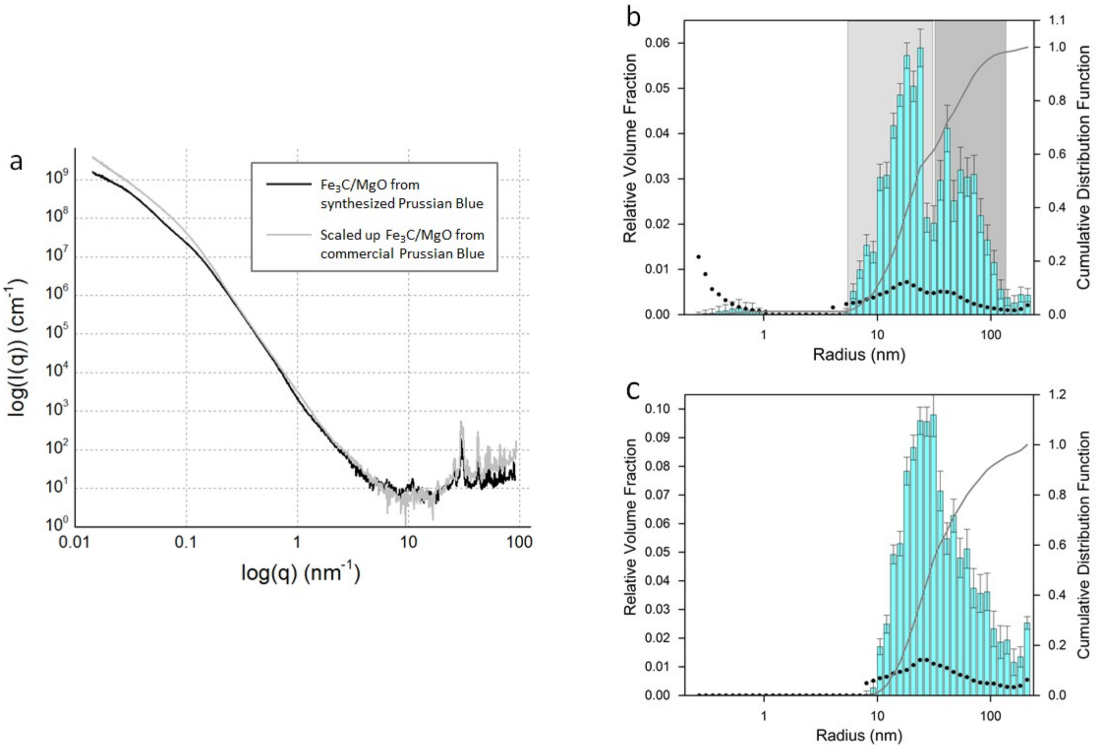

Figure S8 a) SAXS and WAXS data for samples of Fe_3C/MgO prepared from as-synthesized Prussian blue and commercial Prussian blue (larger scale synthesis). Also corresponding size distribution histograms for b) the small scale and c) large scale samples.

2.6 Preparation of a ferrofluid

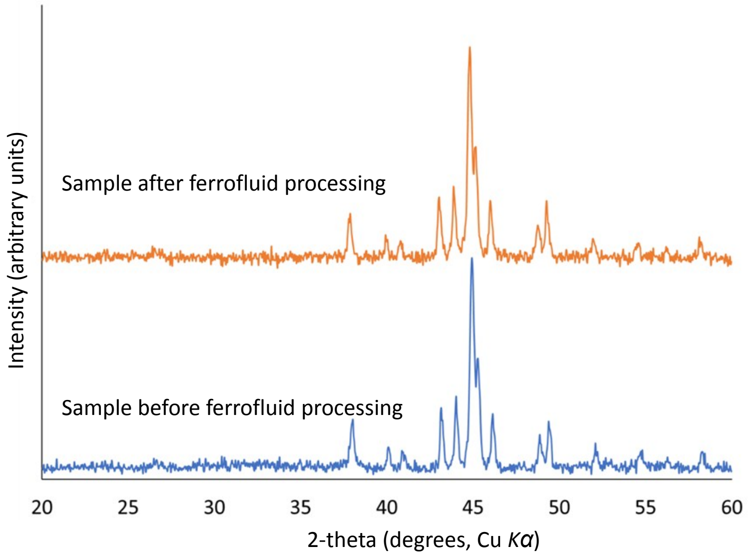

Figure S9 *X-ray diffraction patterns of* Fe_3C *sample before and after processing to produce a ferrofluid, showing that there is no effect on the crystalline material from the ferrofluid preparation method.*

References

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[1] J. Filik, A.W. Ashton, P.C.Y. Chang, P.A. Chater, S.J. Day, M. Drakopoulos, M.W. Gerring et al., Processing two-dimensional X-ray diffraction and small-angle scattering data in DAWN 2, Journal of applied crystallography 50 (2017) 959–966.

[2] B.R. Pauw, A.J. Smith, T. Snow, N.J. Terrill, A.F. Thünemann, The modular small-angle X-ray scattering data correction sequence, Journal of applied crystallography 50 (2017) 1800–1811.