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Authors	Li, Zhonglai;Godsell, Jeffrey F.;O'Byrne, Justin P.;Petkov, Nikolay;Morris, Michael A.;Roy, Saibal;Holmes, Justin D.
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Supercritical Fluid Synthesis of Magnetic Hexagonal Nanoplatelets of Magnetite

Zhonglai Li^a, Jeffrey F. Godsell^b, Justin P. O'Bryne^a, Nikolay Petkov^c, Michael A. Morris^a, Saibal Roy^b and Justin D. Holmes^{a*}

^a *Materials and Supercritical Fluids Group, Department of Chemistry and the Tyndall National Institute, University College Cork, Lee Maltings, Cork, Ireland and the Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), Trinity College Dublin, Dublin 2, Ireland*

^b *Microsystems Centre, Tyndall National Institute, University College Cork, Lee Maltings, Prospect Row, Cork, Ireland*

^c *Electron Microscopy and Analysis Facility (EMAF), Tyndall National Institute, University College Cork, Lee Maltings, Prospect Row, Cork, Ireland*

RECEIVED DATE (automatically inserted by publisher); j.holmes@ucc.ie

The properties of nanomaterials have been shown to strongly depend on their morphology, microstructure, dimensions and crystallinity.^{1,2} Nanostructured iron oxides have been investigated by several research groups due to their potential applications in high-density recording media, ferrofluids and magnetic sensors.³ Various morphologies, including nanowires, size monodispersed nanoparticles and nanostructures encapsulated in carbon nanotubes⁴ have been prepared and investigated using different synthetic methods. For example, Suslick and co-workers successfully synthesized hollow nanosized hematite particles, using carbon nanoparticles as a template, by a sonochemical method.⁵ Recently, ordered mesoporous iron oxide was prepared using a SBA-15 templated approach.⁶ However, to the best of our knowledge, nanostructured cubic Fe₃O₄ with a hexagonal morphology has not been reported to date using any method.

Supercritical fluid (SCF) techniques have been utilized to synthesize various nanomaterials including Ge and Si nanowires and carbon nanotubes.⁷ It is worth noting that supercritical carbon dioxide (sc-CO₂) is often used as a solvent for the formation of nanomaterials due to its negligible surface tension and low viscosity. In this communication we demonstrate for the first time that sc-CO₂ can be used as both a solvent and a reactant to form hexagonal nanoplatelets of Fe₃O₄. The synthesis is based on the thermal decomposition of ferrocene to reduced iron, followed by the subsequent oxidation of the iron particles by sc-CO₂. In a typical SCF experiment, a quartz boat containing 0.5 g of ferrocene was placed in the centre of a high pressure stainless steel reactor (Inconel 625 GR2- Snap-tite, Inc.).⁸ The reactor was then charged with sc-CO₂ ($T_c = 31$ °C, $P_c = 7.38$ MPa) at a temperature of 40 °C and a pressure of 10.34 MPa, and heated to a temperature between 650-750 °C in CO₂, with an outlet flow rate of 200 ml min⁻¹ for 2 h.

The structure of the as-synthesized sample prepared at a temperature of 750 °C and pressure of 10.34 MPa in sc-CO₂ was examined by powder x-ray diffraction (XRD) as shown in Figure 1. Six obvious diffraction peaks can be indexed as the (220), (311), (400), (422), (511) and (440) crystal faces of the cubic phase magnetite (Fe₃O₄). (Joint Committee on Powder Diffraction Standards (JCPDS) File No: 11-0614). The intensities of the three main diffraction peaks correspond well with the JCPDS file, with the refined lattice parameter values of $a = b = c = 8.39$ Å.

In order to more accurately verify the phases, X-ray photoelectron spectroscopy (XPS) analysis of the iron oxide

nanoplatelets was also undertaken (Figure S1 in Supporting Information (SI)). The binding energies relating to Fe 2p_{3/2} and Fe 2p_{1/2} are at approximately 711.3 eV and 724.5 eV respectively, and the broad Fe 2p signals are attributed to the coexistence of Fe³⁺ and Fe²⁺ states.⁹

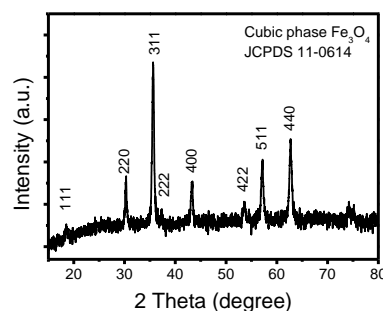


Figure 1. XRD pattern of the iron oxide product prepared at a temperature of 750 °C and a pressure of 10.34 MPa in sc-CO₂.

The morphology of the Fe₃O₄ product obtained is shown in Figure 2. A typical product prepared at 750 °C and 10.34 MPa exhibited well-defined hexagonal nanoplatelets with a mean diameter of 200 nm. The side-view image indicates that the thickness of the nanoplatelets was in the range of *ca.* 20-30 nm. The HRTEM image shows that the lattice spacing is about 0.49 nm, which can be assigned to the (111) plane of Fe₃O₄. It is noteworthy that the synthesized Fe₃O₄ metastable phase is unstable against further oxidation in air at 450 °C for 3 h, whereupon it is transformed to hematite (α -Fe₂O₃). [Figure S2 (a) and (b)].¹⁰ We also investigated the effect of the synthesis temperature on the morphology of the iron oxide nanomaterials, but found that ball-like Fe₃O₄ platelets [Figures S3(a), S3(b)] were produced at temperatures approaching 650 °C instead of the desired hexagonal morphology. Hence isotropic growth of iron oxide occurs at low temperatures in the SCF environment.

Figure 3 shows the magnetic properties of the hexagonal Fe₃O₄ platelets measured at room temperature. The platelets exhibited ferrimagnetic behavior with saturation magnetization (M_s) = 51.4 emu/g, remanent magnetization (M_r) = 18.9 emu/g and coercivity (H_c) = 263 Oe. The room temperature ferromagnetic behavior of Fe₃O₄ platelets was expected, since the overall mean diameter of the particles (~200 nm) was above the

single domain size. Additionally, the saturation magnetization and remanent magnetization of Fe_3O_4 prepared at 750 °C is much larger than that of Fe_3O_4 prepared at 650 °C. The saturation magnetization and remanent magnetization of Fe_3O_4 were 31.9 emu/g and 10.7 emu/g, respectively (Figure S4).

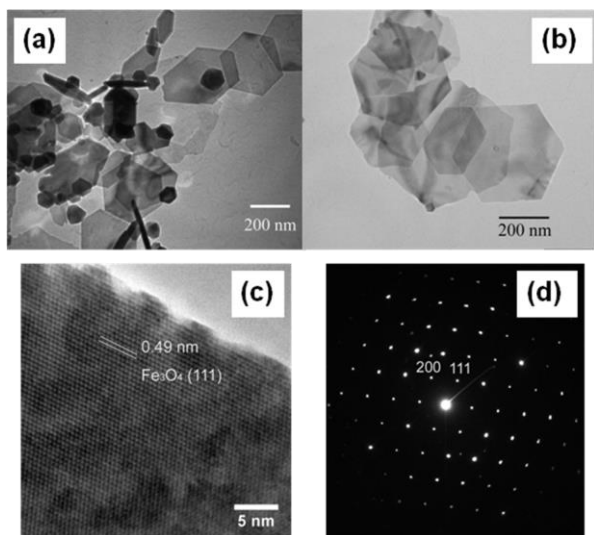
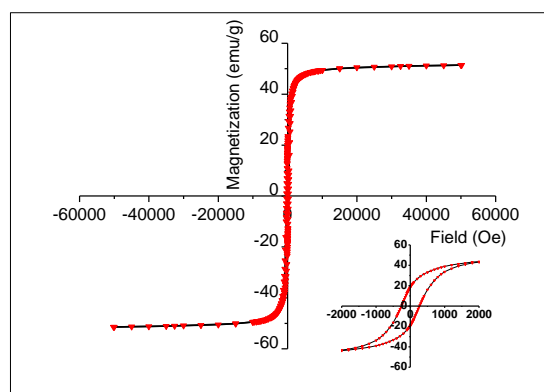


Figure 2. (a) and (b) TEM images, (c) HRTEM image and (d) SAED pattern of the Fe_3O_4 product prepared at 750 °C and 10.34 MPa in sc- CO_2 .

On the other hand, the saturation magnetization value of Fe_3O_4 is less than that for bulk magnetite (92 emu/g) as reported elsewhere.¹¹ The observed lower saturation magnetization value compared to the bulk is possibly attributed in part to an internal compensation within the spinel structure of the A and B magnetic sublattices.¹² The large surface-to-volume ratio of the nanoplatforms, compared to the bulk material, may also be a likely contributing factor to the reduced magnetization. Specifically, the width of the nanoplatforms, being 20–30 nm, is likely to cause spin frustration (spin-glass type) on their surface due to the random canting of surface spins. This phenomenon results in a disorder of the competing superexchange interactions between the Fe tetrahedral and octahedral sites within the unit cells, effectively weakening the overall exchange coupling in the Fe_3O_4



nanoplatforms.

Figure 3. Magnetic hysteresis curve of Fe_3O_4 prepared at a temperature of 750 °C and pressure of 10.34 MPa in sc- CO_2 (inset showing the hysteresis loop zoomed in at the origin).

Ferrocene has previously been used as a precursor to synthesize carbon nanotubes and carbon-coated iron nanoparticles by chemical vapor and supercritical fluid deposition.¹³ Fe particles formed by the thermal decomposition of ferrocene is able

to catalytically generate carbons. In our experiments, undertaken in the presence of CO_2 , it is assumed that the ferrocene first decomposes to form iron nanoparticles when heated above 600 °C.¹⁴ The Fe nanoparticles formed react with sc- CO_2 to form the magnetite platelets, probably through aggregation, as Fe can reduce CO_2 to form iron oxide and CO .¹⁵ In addition any carbon by-products formed can react with CO_2 to form CO .

In summary, we report the preparation of hexagonal magnetite nanoplatforms using a SCF method. CO_2 under supercritical fluid conditions is believed to serve as both a solvent and an oxygen source. Sc- CO_2 and reaction temperature play important roles in the formation of magnetic hexagonal nanoplatforms of magnetite. The obtained magnetic nanomaterial may have potential applications in recording media and sensor devices.

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Supporting Information Available: The XPS, TEM and XRD and magnetic measurement results of products are available in the supporting information.

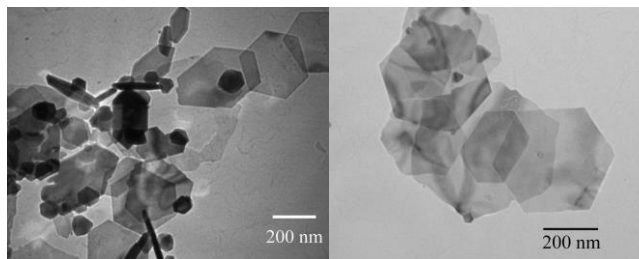
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Figure Caption



ABSTRACT FOR WEB PUBLICATION. A supercritical fluid technique was used to prepare hexagonal nanoplatelets of magnetite. Ferrocene was used as the Fe source and sc-CO₂ acted as both a solvent and oxygen source in the process. XRD, TEM, XPS and magnetic measurements were used to characterize the products. It was found that the morphology and structure of the product strongly depended on the reaction conditions.
