Supporting Information for

Monodisperse magnetite nanoparticles with nearly ideal saturation magnetization

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Iron oleate synthesis and effects of workup on nanoparticle morphology

Upon scaling iron oxide nanoparticle synthesis from 2.5 to 40 mmol of iron per batch, we initially noticed large variations in the dispersity and morphology of the nanoparticles. In some cases cubes, rods, triangles and/or plates contaminated the resulting nanoparticles. Since each batch of iron oleate was used to perform multiple thermolysis runs, it soon became apparent that variations in the iron oleate synthesis protocol resulted in large differences in the morphology of the resulting nanoparticles.

We initially had been synthesizing iron oleate at room temperature following a known procedure {Jana:2004kl} and the resulting solution of iron oleate in hexanes after extraction was concentrated by rotary evaporation at 50 °C using a house vacuum system over about an hour. Iron oleate prepared via this method typically gave good quality particles. When the concentration procedure was changed to evaporating the hexanes at 25 °C and 20 mmHg, the resulting iron oleate failed to produce quality nanoparticles.

In order to better understand the effect of temperature and time on the viability of the iron oleate, several different iron oleate preparations were utilized and evaluated. Synthesis of iron oleate at room temperature for 4 hrs, 18 hrs or 65 hrs, followed by standard work-up and concentration at room temperature, all produced an iron oleate which gave poor particle morphology and/or size distribution. Evaluation of reflux (57 °C) conditions for 18 hrs produced solids during the work-up which complicated the extraction procedure. Iron oleate produced at reflux for 4 hrs followed by stirring at room temperature for 15 hrs decomposed to form good nanoparticles sometimes, but not consistently. When the reaction was stirred at room temperature for 16 hrs then heated at reflux for 4 hrs the resulting iron oleate gave very good particles.

For thermolysis at 324 °C in octadecene, Iron oleate made using the conditions described in {Park:2004jf}, namely synthesis at reflux for 4 hours, followed by immediate work-up, routinely gave the most monodispersed

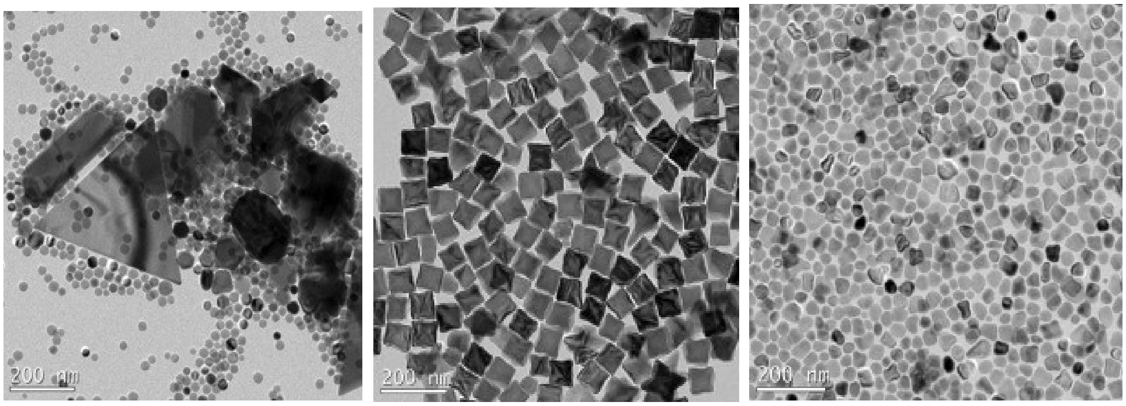


Figure S1. Examples of nanoparticles resulting from nonoptimal iron oleate.

nanoparticles, free of contaminating shapes. These results lead us to believe iron(III) oleate forms multiple structures, not all favorable for nanoparticle synthesis, and the preferred structure is formed upon heating at reflux, but slowly transforms to less desirable forms while stirring the reaction mixture at room temperature. It was also realized the iron oleate mixture contains incorporated water and/or ethanol and oleic acid (free or as ligands) and these components could fluctuate based on even small variations to the procedure, affecting the reproducibility of the resulting nanoparticle size. For example, when the iron oleate solution in hexane was dried with sodium sulfate, extending the drying time from 10 minutes to 45 minutes produced a thickened material which could no longer be gravity filtered. As a precaution, the synthesis of iron oleate was standardized and every aspect of the procedure was strictly adhered to in order to generate consistent batches of iron oleate.

Size reproducibility and stirring control during the nanoparticle formation via thermolysis.

One common problem with scaling up reactions is the change in heat transfer rates related to volume to surface area increase and stirring efficiency. In some instances, we observed side by side reactions with identical reaction mixtures result in different size outcomes. Even though the stir plates were the same model and both set to the same speed, it became apparent the stir plates often stirred at different rates. To confirm stir rate had a significant influence on the resulting size, two reactions were performed side by side (batch 9-156 and 9-157). During the heating and nucleation phases of the thermolysis, one reaction was stirred vigorously (~1000 rpm, such that the center of the stir bar was clearly visible in the bottom of the vortex (~5 cm deep)) and a second reaction was stirred much slower (~300 rpm, the vortex in the center of the reaction was only 1 cm deep). The resulting nanoparticles had a large difference in median diameter: 27.4 nm (sigma = 0.07) for the fast stir rate and 35.9 nm (sigma = 0.08) for the slow stir rate. This dramatic difference in size clearly indicated stirring control is critical to obtain size reproducibility.

TLC Analysis of thermolysis reaction mixture for oleic acid ketonization by-product and isolation of fatty ketones.

In order to determine the extent of ketonization during a thermolysis reaction the following procedure was used: Technical grade oleic acid (90%) was used. A standard thermolysis reaction was perform on 40 mmol of Fe using 7.2:1 oleic acid ratio and halting the reaction 1 hr after the turbidity event. From this reaction mixture a 10 mL sample (about 1/37th of the total) was taken. The black solution was diluted with heptane (10 mL), ethyl acetate (20 mL) and acetone (3 mL) and centrifuged to remove the iron oxide nanoparticles. The resulting supernatant solution was concentrated on a rotary evaporator. The material was evaluated by TLC (MerckKGaA TLC Silica gel 60 F254) along with standards of oleic acid and octadecene using dichloromethane/hexanes (1:1) as eluent: TLC showed a pair of high Rf spots determined to be octadecane (Rf = 0.85) and octadecene (Rf = 0.81), followed by the fatty ketones as a mixture of possible products (Rf = 0.64 to 0.36, major spot at 0.43) and traces of unknowns near the baseline. To quantify the amount of ketones in the sample, the material was eluted through silicagel (200 mL) with hexanes (~200 mL) to elute the octadecene and octadecane. The silicagel was then eluted with dichloromethane (~500 mL) which eluted the ketone products. All fractions containing ketones, as determined by TLC analysis, were rechromatographed using dichloromethane/hexanes (1:1) to give a mixture of ketones (2.261 grams). The ketone material was verified by ^{1}H NMR (300 MHz, $DCCl_3$) see Figure S3.

Additional experimental procedures.

Synthesis of Iron(III) oleate as a solution in 1-octadecene.

In some cases for ease of transfer it was desireable to maintain iron oleate as a solution in 1-octadecene. The standard procedure from the publication was modified in the following way: During the work-up, when evaporation of hexane had slowed, 1-octadecene (200 mL) was added and concentrating was continued on a rotary evaporator with high vacuum for about 30 minutes. The iron(III) oleate solution was placed on a high vacuum line overnight. The resulting solution was deemed to contain 160 mmol of iron(III) and 1-octadecene (200 mL) and could be divided by mass for use in the nanoparticle synthesis.

TEM analysis of Iron oxide Nanoparticles.

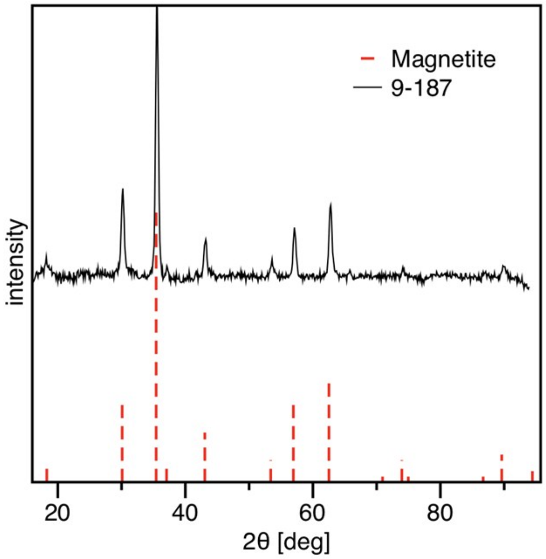
A sample for TEM was prepared with 2 mL of reaction mixture added to a 40 mL vial, followed by the addition of hexanes (3 mL) followed by the addition of ethyl acetate (10 mL). The vial was placed on the edge of a FeNdB permanent magnet, Grade N51 (3" x 3" x 1") for about 10 minutes. The solution was removed from the resulting black solids and the wash procedure was repeated 2 more times. The black nanoparticles (about 10 mg) were dissolved in chloroform (about 2mL), sonicated for a few minutes and 10 microliters of the solution were added, in 3-4 drops from a 10 microliter pipette, to a TEM grid (pure carbon film on 200 mesh copper grid, Ted Pella catalog number 01840-F) for TEM imaging and electron diffraction. TEM size was determined from bright field images acquired with a FEI Technai G2 F20 at 200 kV. Multiple micrographs were analyzed, typically > 3 images acquired from different regions of the grid, with >1000 particles total. Diameter histograms were generated using the particle size analyzer (PSA r12) plugin available for the Imagej software and the results were fit to a log-normal distribution function using Mathematica. Selected area electron diffraction (SAED) patterns were analyzed using the radial integration tool in imagej.

Magnetic Characterization by vibrating sample Magnetometer (VSM).

A 10 mg sample of washed iron oxide nanoparticles were coated with PMAO-PEG co-polymer and phase transferred into water for magnetic characterization. Magnetization versus field measurements were measured at room temperature in a VSM (LakeShore) with fields up to 0.2 T. Magnetic size was determined by fitting the MvH curves to a langevin function using Chantrell's method. Samples contained 100 microliters of nanoparticle-DI water suspension at a typical concentration of 2 g Fe/L.

Iron oxide Nanoparticle washing procedure.

A portion of the crude reaction mixture containing nanoparticles (10 mL) was washed by the addition of ethyl acetate (30 mL). The vial was placed on the edge of a FeNdB permanent magnet, Grade N51 (3" x 3" x 1") for about 10 minutes. The solution was removed from the resulting black solids and the solids were dissolved in heptane (5 mL) with sonication. Ethyl acetate (20 mL) was added and the magnetic separation was repeated. The washing procedure was repeated an additional 2 times. After the last wash, the iron oxide cores were dried under high vacuum for at least 30 minutes to give about 60 mg of iron oxide nanoparticles.



Powder x-ray diffraction of sample NP5

Figure S2. Powder x-ray diffraction of sample NP5(9-187). Diffraction pattern matches magnetite reference pattern.

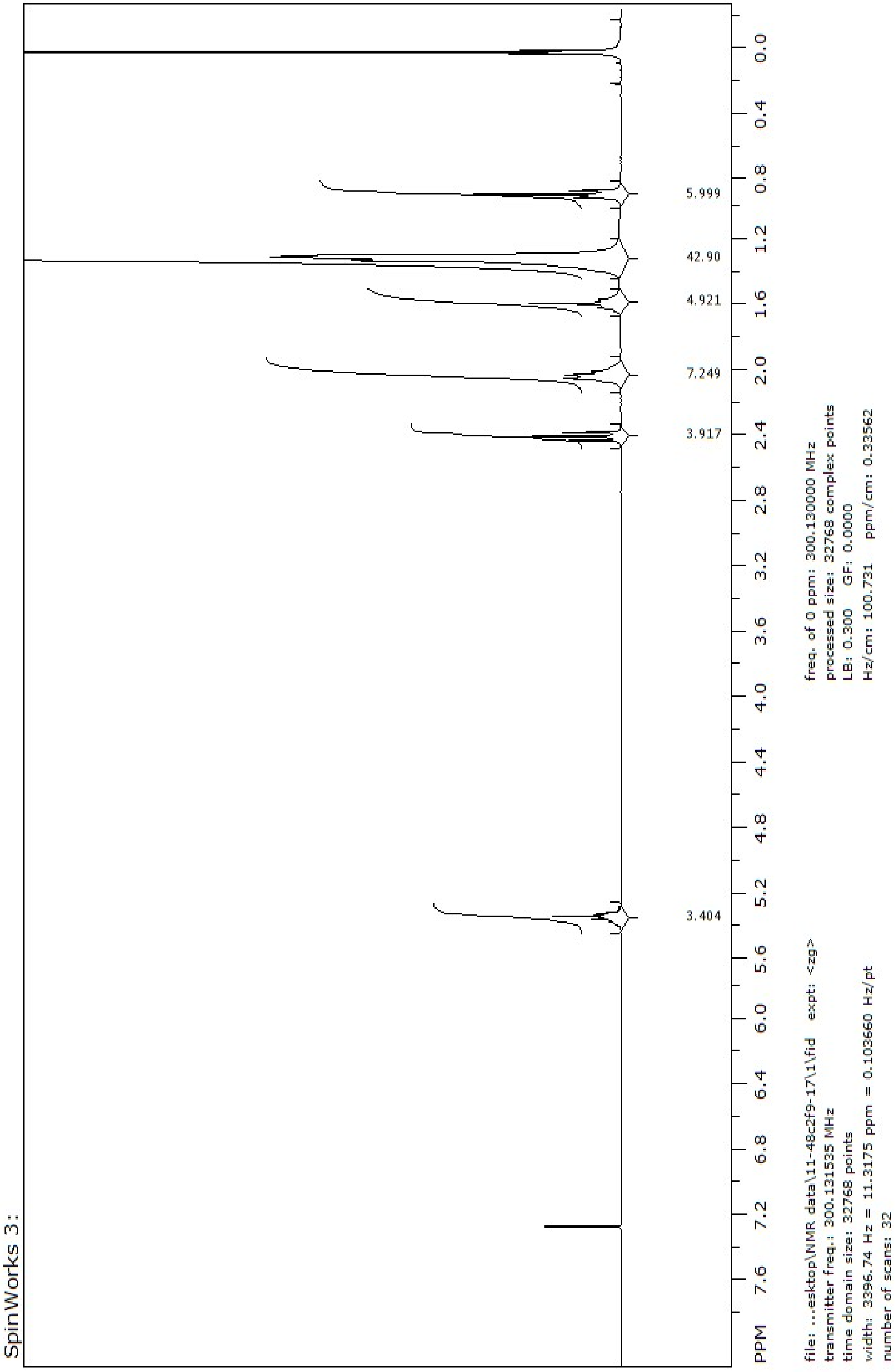


Figure S3: ^{1}H NMR of mixed fatty ketones at 300 MHz.