

Large-Scale Synthesis of Magnetite Powders

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ABSTRACT

This research focuses on a low-cost, large-scale (kg) synthesis of magnetite. Once the base colloid is prepared, there are two distinct routes to synthesizing magnetite powders. The first process dehydrates the colloid *in vacuo*. The solid recovered is then treated thermally (1-12 hrs) at 350-450 °C under a flow of 5% hydrogen in nitrogen. Method two consists of the addition of a reducing agent (NaBH₄, hydrazine) to the colloid followed by the addition of a base (NaOH, KOH, NH₄OH, (Prop)₄NOH) to precipitate the particles out of solution. The particles are then recovered by filtration or centrifugation. In both cases, the resulting solid has been characterized by XRD and identified at 95-99% magnetite, and displays super-paramagnetic behavior. The particle size has been determined by TEM to be 11-20 nm.

Keywords: magnetite, nanoparticles, colloid, large-scale

1 INTRODUCTION

The development of nanoparticles has been intensively pursued not only for the fundamental scientific interest of the materials, but also for a multitude of technological applications[1] including magnetic storage media, ferrofluids.[2], magnetic resonance (MRI) contrast agents, magnetically-guided drug delivery, medical diagnosis, alternating-current (AC) magnetic-field-assisted cancer therapy (hyperthermia)[2], and in various environmental applications such as the degradation of chlorinated hydrocarbons and hard metals in contaminated waters and soils. Various methodologies have been utilized to synthesize magnetite nanoparticles.[3] One common method uses the co-precipitation of mixed ferrous (Fe⁺²) and ferric (Fe⁺³) ions under basic conditions, however the resulting particles have minimal crystallinity.[4] More current work has focused on making crystalline Fe₃O₄ particles of uniform size through a high-temperature reaction of iron(III) acetylacetonate.[5] While some methods have been shown to produce highly crystalline and uniformly sized magnetic nanoparticles, many of these synthetic procedures cannot be applied to large-scale production due to costly starting materials, toxic reagents, rigorous reaction conditions and complex synthetic steps [6]

2 EXPERIMENTAL

Magnetite particles were synthesized on the kilogram scale using two different techniques. First, an aqueous colloidal solution was prepared through the dissolution of metallic iron (Spectrum Chemicals, 1-20%, wt/wt) containing a mixture containing some or all of the following: (hydrochloric acid, glycolic acid, citric acid, acrylic acid, adipic acid, polyacrylic acid) as well as additional stabilizers including some or all of the following (ethylene glycol, polyethylene glycol (350-4000Da), Triton-X100, and aminopropyltriethoxysilane (APTES, Sigma-Aldrich). Once the base colloid is prepared, there are two distinct routes to synthesizing magnetite powders. First, the colloid is dehydrated (hot plate in air, or *in vacuo*). The solid recovered is then treated thermally (1-12 hrs) at 350-450°C under a flow of 5% hydrogen in nitrogen. Method two forms magnetite in solution through the addition of a 1M reducing agent (NaBH₄, Aldrich), (hydrazine, 35%, Aldrich) to the colloid followed by reflux in alkaline media (KOH, NH₄OH, (Prop)₄NOH). The pH is kept between 9.0-9.5 and the resulting particles were recovered by filtration or centrifugation.

3 RESULTS AND DISCUSSION

The black iron oxide particles recovered were then characterized by XRD for phase determination as well as crystallite size. Samples prepared from both methods were run on a Philips PW1800 diffractometer using Cu radiation at 40KV/30mA over the range of 20° to 80° with a step size of 0.03° and a counting time of 12 hours. After collecting the data, the phases present were determined with the aid of the Powder Diffraction File (PDF) published by the International Centre for Diffraction. See table 1 and figure 1.

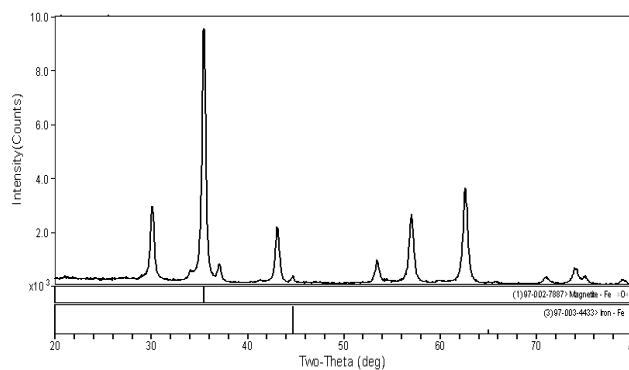


Figure 1: XRD pattern for HW-Fe5

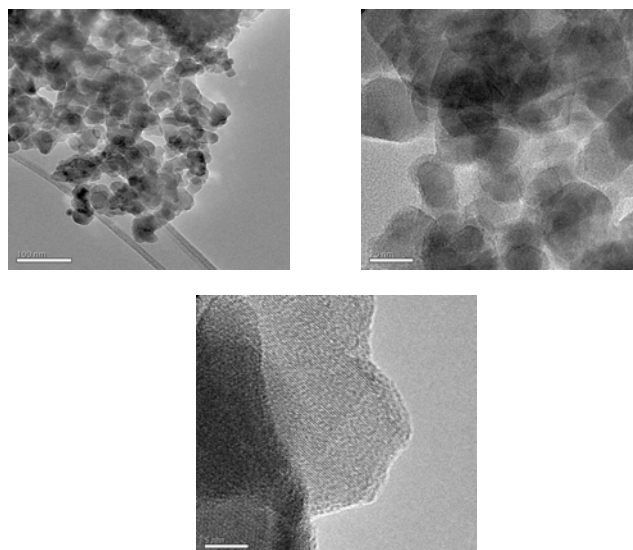


Figure 2a-c: TEM images at increasing magnification

Weight Fraction (wt %) and Domain Size (Å)			
ID	α -Fe ₃ O ₄ (Magnetite)	γ -Fe ₃ O ₄ (Magnetite)	Fe
Method 1: Thermally treated under H ₂			
HW-Fe1	99.8 ± 0.9 189Å		0.2 ± 0.1 392Å
HW-Fe2	93.5 ± 0.8 154Å	6.5 ± 0.1 145Å	
HW-Fe3	100 115Å		
Method 2: Reduced in colloid			
HW-Fe4	92.7 ± 1.2 177Å	2.4 ± 0.2 640Å	
HW-Fe5	93.4 ± 0.5 206Å		0.8 ± 0.1 271Å
HW-Fe6	98.8 ± 1.2 213Å		1.2 ± 0.1 515Å

Table 1: XRD results

As seen in the table above, the vast majority of the powders from either method are in the magnetite phase, and the average crystallite size ranges from 11.5-21.3 nm. The crystallite size is somewhat larger for the solution based reduction. The samples were also examined *via* TEM and micrographs are shown in figure 2a-c. From these images, we can see the diameter of the particles is around 20nm and with increasing magnification the crystal planes of the magnetite particles are clearly visible.

4 CONCLUSIONS

Two distinct routes were used to synthesize kilogram batch quantities of magnetite powders. Both methods resulted primarily in highly crystalline magnetite particles with a mean particle size of 20nm. These results show that a low-cost method for making industrially relevant quantities of magnetite particles has been created.

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