Synthesis of Magnetic Nanoparticles Using Spinning Disc Processing

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ABSTRACT

Spinning disc processing (SDP) has been utilized to modify the aqueous, inverse co-precipitation method for the production of Fe3O4 nanomaterials patented by Massart in 1982 [1]. Size distributions within the 3 to 12 nm range have been produced, with narrow particle size spread, on a rapid, continuous basis. It has been demonstrated that this processing technique results in a general reduction in particle size. Further, the role and limits of applicability of tartaric acid as a surfactant for particle formation control have been established to lie within the range of 1:1 to 10:1, [tartaric] to [Fe], with concentrations in excess resulting in amorphous materials and below this having minimal effect. Marginal, high concentrations have been demonstrated to occasionally result in particles with induced twinning and lattice dislocation defects.

Keywords: SDP; Magnetite; Nanoparticle; co-precipitation; synthesis

1 INTRODUCTION

Traditional commercial wet synthesis techniques for nanomaterial production have inherent and significant shortcomings that are either uneconomical or technically impossible to overcome. These include the inability to produce very narrow size distributions on a continuous basis [1, 2], low throughput, high wastage and significant, process-customized commercial capital requirements.

Despite these shortcomings, magnetic, ferrous nanomaterials have gained enormous interest and focus over the past few decades within the research community [3] and significant progress has been made towards overcoming many technical and process limitations within the field of nanomaterial production [5].

The development of a continuous, rapid production process is of key importance if these materials are to find more common use.

Spinning disc processing (SDP) has previously demonstrated the capability to overcome this key limitation by rapidly and continuously manufacturing $BaSO_4$ nanoparticles in the 700nm range, with demonstrably narrower size distributions than are achievable in the conventional bench top synthesis [5]. The adaptation of this technique to the production of super-paramagnetic (sub-10nm) magnetite nanomaterials has been the focus of this work.

2 BACKGROUND

The process for the binary precipitation of magnetite was first patented by R. Massart in 1982 [1]. Solutions of ferrous and ferric chloride within 1*M* HCl are reacted with an excess of NH_3(aq) or NaOH(aq) and the resulting nanomaterial collected, washed and peptized to achieve a colloidal solution of magnetically active particles. In sufficient concentrations these particles are then able to influence the behavior of the fluid medium suspending them, creating ferrofluids with a range of commercial applications [6]. In addition they find use as additives for polymer manufacture and as the basis for fundamental physical research into magnetism on the nano-scale.

The limitations of this process are that the product has wide size distributions and poor selectivity for desirable particle characteristics. Extensive centrifugal classification is required to achieve the narrow size distributions seen for similar products generated by the synthesis using the decomposition route. This has resulted in this technique only receiving limited attention within the nanotechnology field.

The enhanced mixing characteristics and fine reaction duration and rate control possible using SDP techniques has been utilized to improve upon these limitations, with demonstrably narrow size distributions resulting. In addition, production with this technique requires a single-multi-function processor and is continuous with high rates of throughput.

3 SDP CHARACTERISTICS AND OPERATION

Spinning disc processing (Figure 1) uses a rapidly rotating (5-3000rpm) stainless steel disc onto which reagents can be delivered through a number of different jets. Highly effective turbulent micro-mixing occurs as the

reagents propagate across the surface of the disc under the influence of centrifugal forces.

The reaction temperature is controlled by a recirculation coolant system that permits both heating and cooling of the disc surface. Both smooth and grooved stainless steel discs can be utilized for operation though the grooved discs have demonstrably superior wetting characteristics.

The reactant solutions are delivered to the centre of the rotating disc where they are accelerated by viscous drag until an inverse hydrostatic jump occurs and the fluid layer spreads across the disc in a 10-200µm layer. This thin, rapidly moving layer provides very effective heat exchange with the surface of the disc and mass exchange with the atmosphere above the disc.

Effective throughputs for the SDP used range from 0.5 to 3ml/s for low viscosity solvents delivered using continuous gear pumps and residence times within the reactor are commonly less than 1 second. Lower feeds and/or disc speeds are prone to form rivulets rather than the requisite fluid film, whilst larger feed rates will require too large a spin up zone.

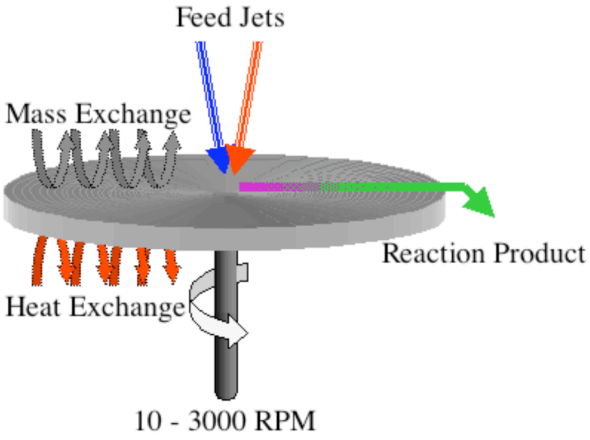

Figure 1: Schematic of spinning disc processing

4 METHODOLOGY

Aqueous solutions of ferrous and ferric chloride (1:2) were prepared in 1*M* deoxygenated HCl with Fe concentrations between 0.01*M* and 1*M*. Tartaric acid was added to these solutions to function as a particle growth control agent, in concentrations ranging between 0.01 and 10*M*.

Aqueous, deoxygenated solutions of NH_3 and NaOH were prepared to function as a counter-reagent in the binary precipitation of magnetite, with concentrations between 1x and 3x the stoichiometric requirement to neutralize the HCl, tartaric acid and fully convert the solvated $Fe^{2/3+}$ to oxide.

Both solutions were continuously fed *via* gear pumps into the SDP at between 250 and 1000µl/s (each), wherein a grooved stainless steel disk was utilized.

Synthesis was performed under a shield of high-purity argon with a flow rate of not less than 10 l/min and at room temperature. The products were collected without air exposure and diluted with distilled water with a conductivity not exceeding 5µS to produce samples suitable for dynamic light scattering (DLS) analysis and transmission electron microscopy (TEM).

No size classification was carried out nor were the particles processed in any way beyond production.

DLS was carried out with a calibrated Malvern ZS Nano Particle size analyzer and the results compared with direct observation using a JEOL3000F Materials TEM. High resolution (HR) imaging was used to assess particle crystallinity and morphology.

5 RESULTS

5.1 Role of Tartaric Acid

The success of the synthesis in producing narrow size distributions of sub-10nm particles has been demonstrated, being strongly influenced by the concentration of tartaric acid employed to control particle growth. Reactants exceeding a 1:1 ratio of total iron concentration (=[Fe]) to tartaric acid completely suppress particle formation, even in high concentrates of NH_3/NaOH, whereas concentrations below 10% of [Fe] were ineffective in controlling particle growth.

Synthesis in the absence of tartaric acid produced broad distributions of irregularly shaped particles as can be seen in Figure 2 for [Fe] = 0.1*M*, using NH_3 as the base.

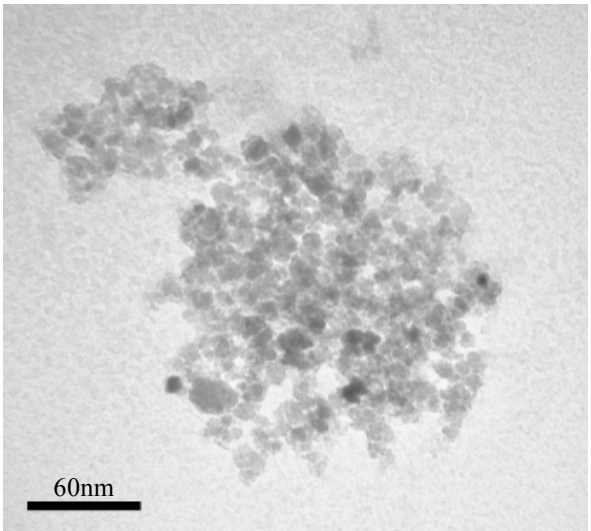

Figure 2: Characteristic TEM micrograph for particles produced from [Fe]=0.1, using NH_3 as base in the absence of tartaric acid.

The addition of 0.1M of tartaric acid can be seen to have a strong effect in reducing the irregularity of the particles and narrowing the size distribution in Figure 3.

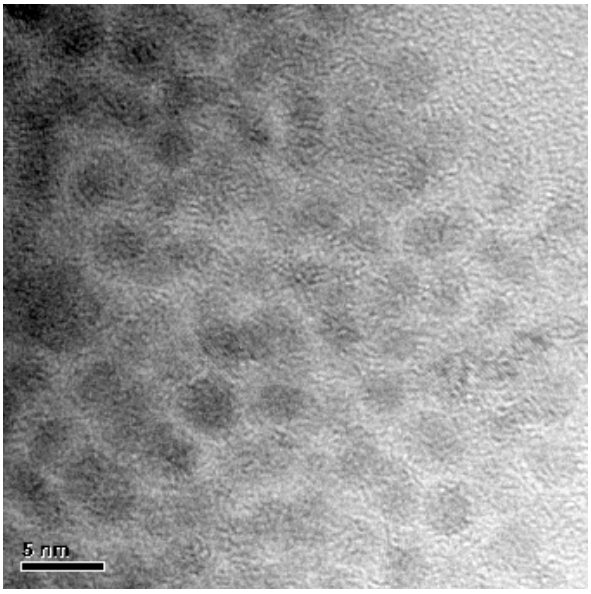

Figure 3: Characteristic TEM micrograph for particles produced from [Fe]= 0.1*M*, using NH_3 as base in the presence of tartaric acid.

5.2 Role of the SDP

Use of SDP resulted in a general reduction in the size of the particles, as seen in Figure 4 for 0.1*M* [Fe] with 0.1*M* tartaric acid. Sizing was performed by manually measuring 100 particles in size calibrated TEM micrographs.

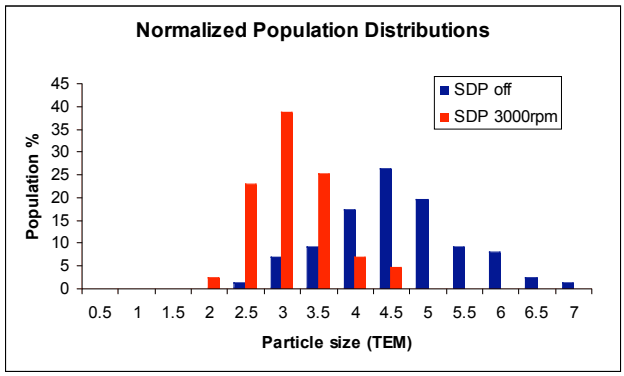

Figure 4: TEM derived population distributions for 0.1*M* [Fe] in 0.1*M* tartaric acid.

Low disc speeds have no effect upon particle size, a result of improper fluid film layer formation upon the disc. Rivulets are often observed upon the disc surface for low flow rates and/or low disk speeds.

High disc speeds (2000-2500rpm) and low [Fe] concentrations favor the formation of populations of very small particles with very narrow size distributions in the presence of sufficient tartaric acid. DLS results demonstrate this for [Fe] = 0.32*M*, [tartaric acid] = 0.32*M* can be seen in Figure 5.

Very high disc speeds (>2500rpm) result in degraded particle population characteristics. The rate of radial motion at these speeds is too fast for the reaction to complete before the reactants leave the disk, resulting in particle ripening after processing.

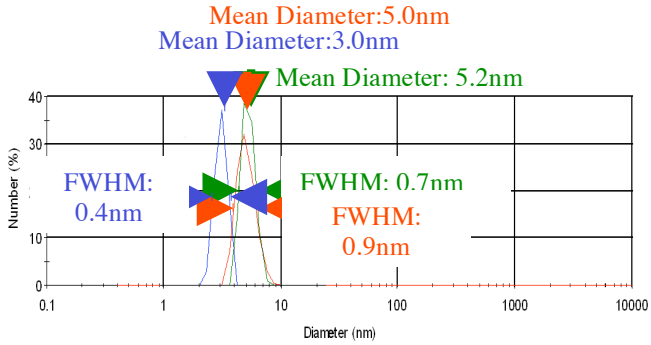

Figure 5: Dynamic Light Scattering particle size distributions for [Fe] = 0.32*M*, [tartaric acid] = 0.32*M*; note the very narrow size ranges present.

A common outcome of synthesis within the SDP was a partial suppression of particle formation, resulting in the formation of amorphous gels rather than discrete crystalline particles. A characteristic image of one such gel can be seen in Figure 6. Whilst iron bearing, these gels were nonmagnetic and varied in size greatly, invalidating DLS as a method for particle size analysis.

Gel formation was more common for syntheses utilizing NH_3 as the base, whereas NaOH was a seen to be more effective at producing crystalline materials.

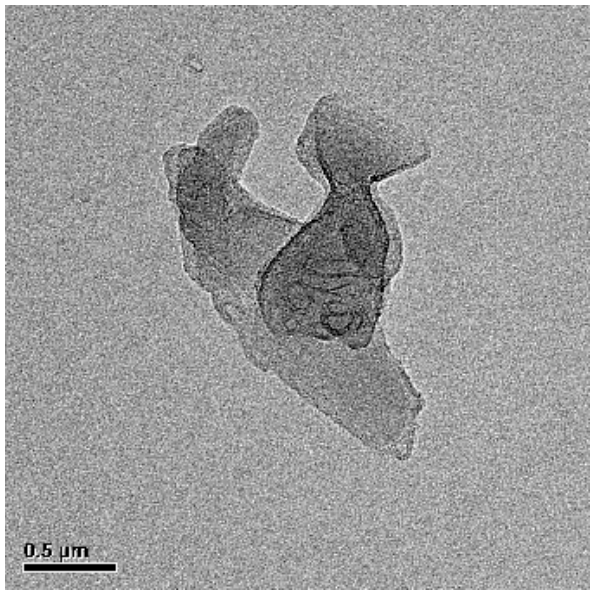

Figure 6: Typical ferrous gel resulting from SDP processing.

Materials produced with oxygenated solvents, large amounts of tartaric acid and using NH_3 as the base occasionally manifested twinning dislocations and lattice defects as can be seen in Figure 7. Only precise conditions produce these defects within the particles, as this is an unstable point in the synthesis. This makes reproducibility poor for these materials.

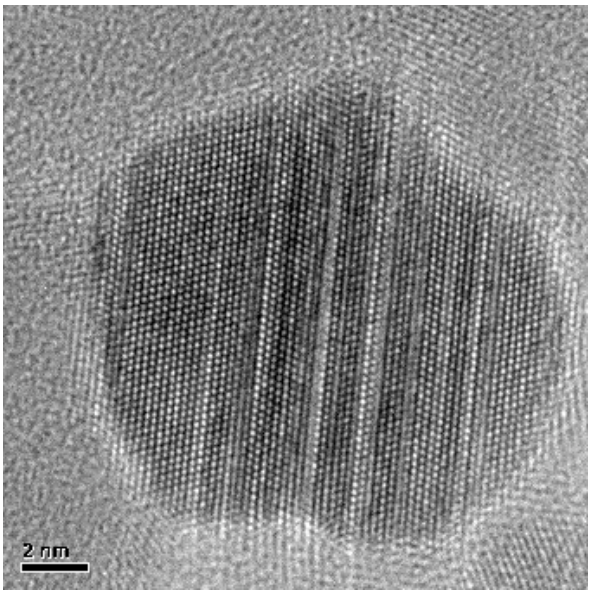

Figure 7: Defects within particle generated under marginal conditions.

6 CONCLUSION

Magnetic nanomaterials have been produced in a range of sizes from 3 to >12nm using a continuous synthesis process based around the use of inverse co-precipitation within a spinning disc processor. The role of tartaric acid as a stabilization/particle growth control agent has been investigated and a viable concentration range of 10-100% of the [Fe] within the starting solution established. Particle formation suppression within the SDP has been demonstrated for concentrations in excess of this and the population characteristics have been observed to converge upon those observed for surfactant free syntheses for concentrations below this range.

The capabilities of SD processing have been demonstrated, including an induced reduction in mean particle size and the ability to produce very small magnetitie nanoparticles in narrow size distributions.

In addition, marginal conditions of high disk speed and high surfactant concentration have been demonstrated to induce defects within nanocrystals of Fe_3O_4.

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