

# Preparation of Nano-Size Magnetic Gamma Ferric Oxide ( $\gamma\text{-Fe}_2\text{O}_3$ ) and Magnetite ( $\text{Fe}_3\text{O}_4$ ) Particles for Toner and Color Imaging Applications

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## Abstract

In the present study, we report a chemical synthesis technique for the preparation of gamma ferric oxide ( $\gamma\text{-Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) particles in the nanometer size range. The particles are produced in powder form by precipitation in the aqueous cores of water-in-oil microemulsions. The latter act as constrained reactors for the precipitation reaction. X-ray diffraction was used to identify the particles and TEM was used for size determination. The magnetization data demonstrate the superparamagnetic behavior of the particles. To prevent the particles from aggregation, the particles were covered with a monolayer of vinyltriacetoxy silane. The nanosize magnetic particles have potential applications in the manufacture of colored magnetic toners.

## Introduction

Synthesis of particles with nanometer size dimensions is of increasing scientific and technical interest.<sup>1</sup> Materials with particles in the nanometer size range exhibit novel electronic, optical, magnetic, and chemical properties due to their extremely small dimensions.<sup>2</sup> These materials may find applications in catalysis<sup>3,4</sup>, optical and electronic devices<sup>5</sup>, and may also serve as valuable precursors for ceramic materials with enhanced mechanical properties.<sup>6</sup> Thus, nanophase ceramics can be stretched at low temperatures (about 1600°C) making them easier to fabricate into objects. Moreover, refractory materials can be processed to form more dense, and potentially fully dense, ceramics from ultrafine nano particles. At room temperatures, these ceramics are also tougher and stronger than their coarser grained cousins.<sup>1</sup> Another material—nanophase titania ( $\text{TiO}_2$ )—is a more efficient catalyst for sulfur removal than are conventional forms of titania.<sup>1</sup>

Although several studies have been devoted to the synthesis of nanophase semiconductors, ceramics, and catalysts, relatively little work exists for magnetic particles in the nanometer size range. Unlike ordinary magnetic materials, nanometer-sized magnetic particles enjoy two new

properties: (i) superparamagnetism, and (ii) optical transparency. Both properties are a consequence of the small size of the particles. The first property—superparamagnetism—implies that the particles cannot be magnetized permanently at room temperatures and are thus only magnetic in the presence of an outside magnetic field. This means they will not stick to each other, which could make the particles useful as a high-definition toner for photocopying machines, magnetic memories for computers, magnetic fluids, and magnetic refrigeration. The transparency of the particles is an added bonus, not usually found in ordinary magnetic materials at room temperature. In this new state, the nanoparticles have potential applications in the manufacture of magnetic toner for color copiers. To magnetize a toner, one typically mixes the ingredients with magnetic materials like magnetite ( $\text{Fe}_3\text{O}_4$ ), which is black, or bulk  $\gamma\text{-Fe}_2\text{O}_3$ , which is brown. The product tends to be a dark or muddy-looking pigment, and the color is highly distorted. Mixing instead transparent magnetic particles with a pigment would produce bright colors which would enhance the quality of color copies in color copiers and laser printers.

A major obstacle during the synthesis of nanosize particles using conventional chemical methods is the tendency of the particles to aggregate in solution in order to reduce the energy associated with the high ratio of surface area to volume. The problem was overcome by Ziolo et al.<sup>7-8</sup> who succeeded in forming nanocrystals of gamma ferric oxide ( $\gamma\text{-Fe}_2\text{O}_3$ ) in the porous network of an ion-exchange resin. The resin was used to constrain the reaction environment and to isolate and stabilize the particles during their formation. The  $\gamma\text{-Fe}_2\text{O}_3$  nanocrystals were prepared using a Dowex ion-exchange resin containing sulfonate groups. The  $\text{Na}^+$  and  $\text{H}^+$  ions associated with the sulfonates are easily exchanged with  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ . Addition of concentrated sodium hydroxide produces iron hydroxides, which are then converted to  $\gamma\text{-Fe}_2\text{O}_3$  using hydrogen peroxide or hydrazine. The oxide particles were found to be uniformly and densely distributed throughout the polymer matrix. The matrix, of course, plays a critical role in controlling the growth of the nanocrystals by imposing a limit on their size and also in

keeping the particles isolated by providing spatially localized sites for their formation.

Using Ziolo's synthesis method, the nanocomposite is produced in the form of clear, amber colored resin beads about 50 to 100  $\mu\text{m}$  in diameter. These beads are much too large to be used in toner or some other imaging application.<sup>9</sup> Although the beads were found to be "tremendously resilient" and resisted being broken down into a powder, multiple loadings and adding more iron to the reaction system results in resin beads that contain so many  $\gamma\text{-Fe}_2\text{O}_3$  particles that the beads begin to crumple on their own.<sup>1</sup> By milling these weakened beads with water, one obtains an aqueous ferrofluid with the same magnetic and optical properties as those of the nanocomposite beads. This aqueous ferrofluid is again unsuitable for toner or other imaging applications.

For toner and color imaging applications, it appears necessary to have the nanosize magnetic particles in powder form so that they can be readily mixed with the pigments. This is the objective of the present study. Nanoparticles of maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) are produced in powder form by precipitation inside the aqueous cores of water-in-oil microemulsions. To prevent the particles from aggregation, the particles are covered with a monolayer of vinyltriacetoxysilane. Following this procedure, magnetic particles of nanometer size can be produced in powder form.

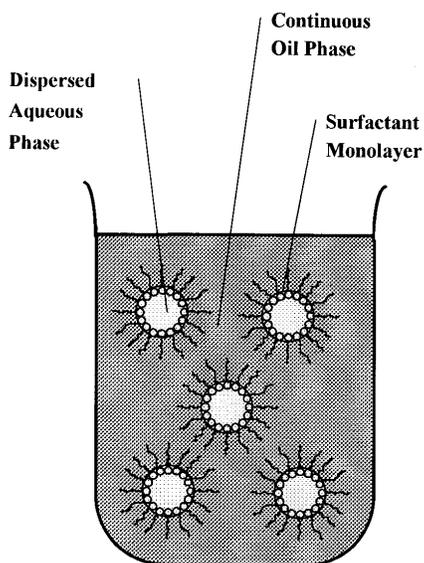


Figure 1. Water-in-Oil Microemulsion.

### Microemulsions as Microreactors

A microemulsion is generally defined as a thermodynamically stable isotropic dispersion of two immiscible liquids consisting of one or both liquids stabilized by an interfacial film of surface active molecules. In water-in-oil microemulsions, the aqueous phase is dispersed as nanosize droplets (typically 5 - 25 nm in size) surrounded by a monolayer of surfactant and co-surfactant molecules in the continuous hydrocarbon phase (see Figure 1). If a water-soluble metal salt is incorporated in the aqueous phase of the microemulsion, it will reside in the aqueous droplets sur-

rounded by the oil (continuous phase). These aqueous droplets continually collide, coalesce and de-coalesce, resulting in a continuous exchange of solute content. Conceptually, if two reactants A and B are dissolved in the aqueous cores of two identical water-in-oil microemulsions, upon mixing, they will form AB complex and precipitate (see Figure 2). The chemical reaction between the two reactants A and B is controlled by the rate of coalescence of droplets and inter-droplet exchange. Since the two microemulsions (I and II) are of identical compositions, differing only in the nature of the aqueous phase, the microemulsion does not get destabilized upon mixing. The aqueous droplets act as constrained nanosize reactors for the precipitation reaction, as the surfactant monolayer provides a barrier restricting the growth of the particles. This surfactant monolayer also hinders coagulation of the particles. A schematic representation of this process is shown in Figure 2.

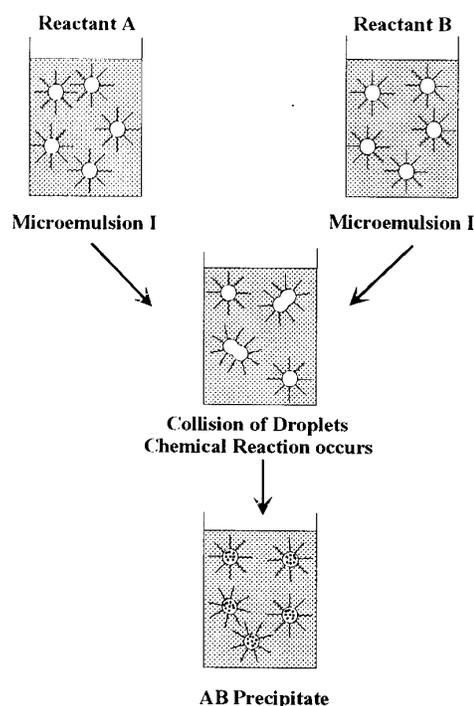


Figure 2. Reaction in Microemulsion.

A microemulsion consisting of sodium dodecyl sulfate (SDS) as surfactant, aerosol OT (AOT) as cosurfactant, and isoctane as the continuous phase. This system solubilizes a fairly large volume of water producing stable, transparent, single phase systems. The size of the aqueous droplets of these microemulsion systems was determined by Quasi-Elastic Light Scattering (QELS).

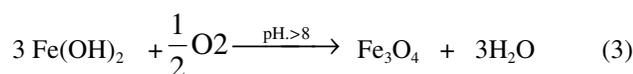
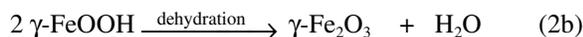
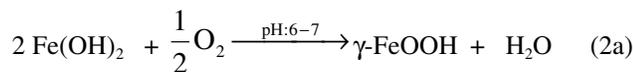
### Synthesis of Maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) and Magnetite ( $\text{Fe}_3\text{O}_4$ ) Nano Particles

Maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) can be produced via the oxidative hydrolysis of  $\text{Fe}^{2+}$  solutions.<sup>10</sup> The end product depends on the pH of the solution and the reaction conditions. The synthesis route follows the following reactions:

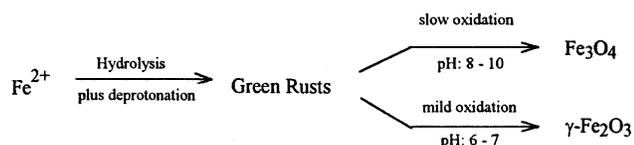
Hydrolysis plus deprotonation:



Oxidation plus dehydration:



Since hydrolysis releases protons, it is necessary to add a base to the system in order for the pH to remain constant during the reaction. Potassium and sodium hydroxides buffered with sodium or ammonium nitrate are commonly used. It is preferable, however, to use an organic instead of an inorganic base because of its ability to dissolve in both aqueous and nonaqueous solvents and to maintain the pH within the desired range of 8 to 10. Furthermore, the hydrolysis reaction as written above is an oversimplification. In reality, the reaction results in the formation of an intermediate green complex of the form  $\text{Fe}(\text{OH})_x^{3-x}$ . The latter is unstable and quickly results in the formation of a bluish-green precipitate, commonly known as green rust. Green rusts are not oxides or hydroxides in a strict sense but contain anions as an essential structural component. They consist of hexagonally close packed layers of the  $\text{Fe}(\text{OH})_2$  type with the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in the interstices.  $\text{Fe}^{3+}$  gives the layers a positive charge which is balanced by an intercalation of anions between the layers. Forms with chloride and sulfate anions may have  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios of up to 4.<sup>10</sup> Misawa et al.<sup>11-12</sup> have identified two forms of green rusts which they termed Green rust I and Green rust II. According to these authors, Green rust I is formed in chloride solutions whereas Green rust II is formed in sulfate solutions. The former has an  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio of 2 while the latter has an  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio of unity. Misawa et al. also claim that green rusts have both hexagonal and cubic components of oxygen packing. Since exact forms and compositions of green rusts are not known, no such distinction will be followed here. The oxidation of green rusts results in the formation of  $\gamma\text{-Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$  depending on the pH of the solution and the oxidation rate. Slow aerial oxidation in slightly basic solutions (pH: 8-10) results in the formation of magnetite. While mild oxidation in neutral or slightly acidic solutions (pH: 6-7) results in the formation of  $\gamma\text{-Fe}_2\text{O}_3$ . Accordingly, the formation of  $\gamma\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  from  $\text{Fe}^{2+}$  solution can be represented as:



For the synthesis of magnetite ( $\text{Fe}_3\text{O}_4$ ), ferrous chloride tetra hydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) is dissolved in the aqueous phase of a microemulsion. Next, triethylamine (TEA) solu-

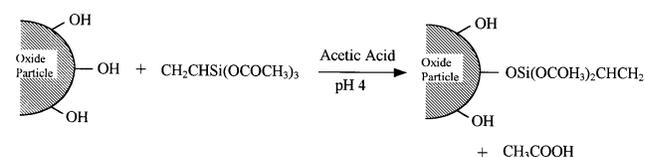
tion in isoctane is added to this microemulsion. Addition of TEA results in the precipitation of Green Rust I. Slow oxidation of Green Rust I in the pH range of 8-10 results in the formation of magnetite.

We should point out that the use of an organic base (TEA) allows the process to be easily controllable and should prove easier than previously used potassium or sodium hydroxide solutions buffered with either potassium or ammonium nitrate. Moreover, since TEA is soluble in both the aqueous and organic phases, this removes the need for a second microemulsion which simplifies the process immensely.

For the synthesis of  $\gamma\text{-Fe}_2\text{O}_3$ , ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) is dissolved in the aqueous phase of a microemulsion. TEA dissolved in octane is next added to this microemulsion. This results in the hydrolysis of  $\text{Fe}^{2+}$  ions and precipitation of iron hydroxides by the diffusion of TEA through the surfactant monolayer and subsequent collision of the droplets. The oxidation of the iron hydroxides to  $\gamma\text{-Fe}_2\text{O}_3$  is carried out using sodium nitrite. To this end, another micro-emulsion containing sodium nitrite as the dispersed aqueous phase (and having the same composition as the first microemulsion) is added to the first microemulsion. The suspension may be heated to about  $50^\circ\text{C}$  in order to enhance the formation rate of  $\gamma\text{-Fe}_2\text{O}_3$ .

## Hydrophobic Treatment of the Particles

The particles can be separated from the microemulsion by first adding water to break the microemulsion. Next, the particles are separated from the aqueous phase by high speed centrifugation. In powder form, however, the particles tend to aggregate because of their tendency to reduce the energy associated with the high ratio of surface area to volume. It is therefore necessary to render the particles hydrophobic by treating the particles in solution before centrifugation. This can be achieved by attaching hydrocarbon groups to the surface of the particles. In this respect, we may note that the particles are characterized by the presence of hydroxyl (OH) groups covering their surface. This is because most oxides in solution have adsorbed water of hydration at their outermost layer. The surface hydroxyl groups can be made to react with vinyltriacetoxysilane (VTAS) according to the following reaction:



Substantial coverage of the particle surface by the vinyl groups will render the particles hydrophobic and prevent particle aggregation.

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