

Characterization of Bio-synthesized Magnetic Nanoparticles

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Abstract— Magnetic nanoparticles have potential utility in a variety of applications ranging from ferrofluids to highly sensitive transduction mechanisms for monitoring and controlling biological activities at the molecular level. This paper describes a novel methodology for bacterial synthesis of a wide range of magnetite-based magnetic nanoparticles. First, this approach is highly scalable and low cost enabling production of large volumes of nanoparticles. Second, like the chemical co-precipitation technique, biologically synthesized materials have the ability to dope magnetite with a wide range of elements enabling fine control over magnetic and thermal properties of the particles. Third, unlike chemical co-precipitation techniques which restrict particle sizes below 20 nm, bacterial synthesis enables control of particle sizes from 10 nm to 100 nm. Finally, we show that some forms of the bio-synthesized materials have a significantly higher saturation magnetization than typical chemically synthesized materials.

I. INTRODUCTION

THE focus of this paper is on the bacterial synthesis of the magnetic nanoparticles. Traditional approaches to synthesizing magnetic nanoparticles generally rely on either solid phase reduction (ball milling) or wet methods (chemical co-precipitation).[1],[2],[3],[4],[5] Both of these approaches have distinct advantages and disadvantages. The basic materials and equipment for ball milling are readily available and easy to use. The disadvantage is consistency and time. The wet grinding process generally requires over 1000 hours, in addition, the process generally requires high temperature (>600 C) which has additional disadvantages to be discussed shortly.[1] Likewise, chemical co-precipitation is relatively straightforward in terms of the chemistry.

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Furthermore, there are a number of procedures in the literature for the addition of other metals for controlling the magnetic and thermal properties of the particles.[6],[7],[8],[9] However, the volumetric production rate is generally low and time consuming (labor intensive) and selectivity of particle size is limited. New approaches to particle synthesis, such as deposition and plasma synthesis, attempt to address limitations of the conventional approaches.[10][11][12]

There has been renewed interest in the synthesis of magnetic nanoparticles. This is partly due to accelerated interest (and funding) in nanotechnology, the ability to integrate nanoparticles with other media, and advancements in material science that enables new compounds that are opening potentially new research areas and applications. Nanoparticles loaded in fluids include a surfactant bound to the surface of the nanoparticle. This surfactant has two roles. First, it provides a barrier between particles to prevent agglomeration. Second, the tails of the surfactant are either hydrophobic or hydrophilic to encourage integration of the particle into the carrier fluid. Recent work has explored alternative surfactants that enable selectivity in terms of binding the particle to cell walls.[13] This ability to selectively bind magnetic nanoparticles to a wide variety of materials opens up numerous possibilities in the areas of medicine and pharmaceuticals as well as detection and/or manipulation of biological activity at the cellular level.[14],[15],[16]

These advancements in materials impact not only future applications of nanoparticles, but enable past applications that were not feasible due to cost and material limitations. To date, almost all applications of ferrofluids (fluids loaded with magnetic nanoparticles) have depended primarily on magnetite. However, recent advancements in the material synthesis area opens new possibilities in terms applications due to finer control of the particle size as well as thermal and magnetic properties. One specific example of how new materials enable an old technology is the magnetocaloric pump. A magnetocaloric pump, first described by Rosensweig[17], exploits the thermal/magnetic behavior of ferrofluids and enables pumping fluid through coincident thermal and magnetic fields. The basic principle, shown in Figure 1, is very simple. Cool ferrofluid is attracted to a magnetic field. As the fluid is drawn into the magnetic field, a coincident heat source warms the fluid. As the fluid heats up,

it loses its attraction to the magnetic field and is displaced by cooler fluid.

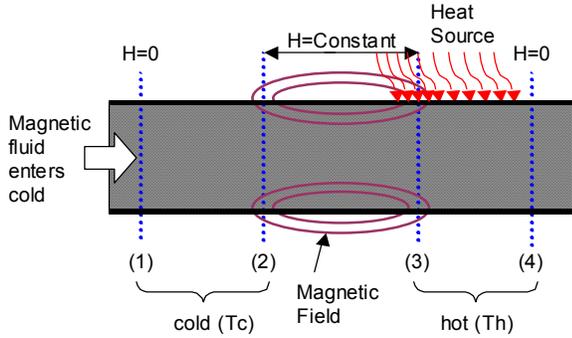


Fig. 1: Magnetocaloric Pump

The key to this pump is the thermal/magnetic behavior of the fluid. Magnetic materials lose their attraction to magnetic fields as temperature rises (see Fig. 2). The Curie temperature is the temperature at which the magnet completely loses its attraction to external fields. Clearly, the ideal pump would have a fluid in which the maximum operating temperature approached the Curie temperature

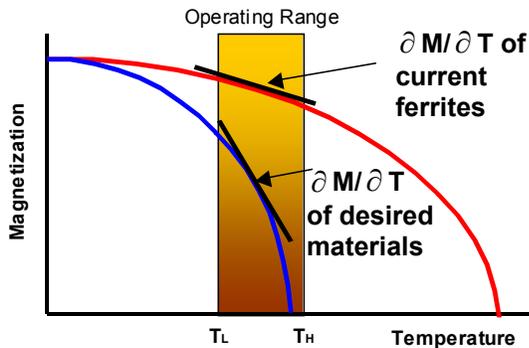


Fig. 2: Thermomagnetic Behavior of Magnetic Materials

Unfortunately, most conventional ferrofluids use magnetite (Fe_3O_4) nanoparticles which have a Curie temperature of 868°K . Subsequently, a pump operating below the boiling point of water is unlikely to produce enough pressure to overcome viscous drag making the magnetocaloric pump impractical. Recent efforts have focused on doping magnetite to modify the magnetization and Curie temperature. Figures 3 compares the temperature variation of conventional magnetite based ferrofluids and a MnZn doped magnetite based ferrofluid. Clearly the introduction of Manganese and/or Zinc into the magnetite lattice appears to significantly impact the material's sensitivity to temperature which subsequently increases the potential pumping pressure. We recently demonstrated how one could increase flow rate by more than an order of magnitude through modifying the particles loaded in the same

fluid. Furthermore, it was demonstrated how this basic methodology could be easily scaled down to the lab-on-a-chip scale.[18]

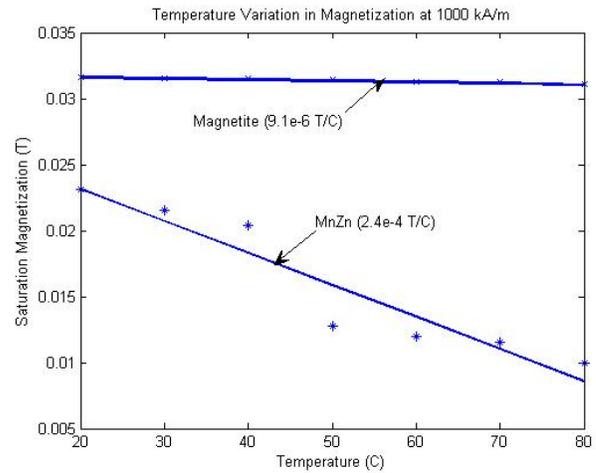


Fig. 3: Temperature variation of magnetization of fluid

II. BACTERIAL SYNTHESIS

In terms of actual particle synthesis, bacterially mediated production is not new. A survey of the literature showed that iron-reducing bacteria have been found in various natural environments including freshwater and marine environments, clean and contaminated aquifers, geothermal vents and deep subsurface environments.[19] Magnetite is a common end product of bacterial iron reduction and has led to many interesting observations in terms of understanding geological settings both on earth as well as other planets.[20],[21] One example of the interesting relationship between bacteria and magnetic nanoparticles are magnetotactic bacteria. Magnetotactic bacteria comprise a number of strains that are indigenous in chemically-stratified water columns. Each cell has inside its body a number of magnetite or greigite nanoparticles. The exact reason why these bacteria contain these nanoparticles is still under investigation, but the bacteria are known to migrate and orient themselves along magnetic field lines.[22] The use of these bacteria as a source of magnetic nanoparticles is not feasible due to the requirement of harvesting the particles from the cells.

Iron biomineralization is commonly divided into two modes: biologically controlled mineralization in which bacteria genetically control the mineralization process (such as the above magnetotactic bacteria) and biologically induced mineralization in which bacteria facilitate magnetite formation by creating external chemical environments suitable for the formation and precipitation of magnetite. The bacteria discussed in the following (shown in Fig. 4) fall under the latter approach in which magnetic nanoparticles are formed

extracellularly as a byproduct of bacterial iron reduction.[23],[24] There have traditionally been a number of advantages, in terms of particle synthesis, of the biologically induced approach over the biologically controlled. First, as pointed out previously, the crystals are produced extracellularly which means that the particles are easily separated from the organisms without requiring the destruction of the organisms. The bacteria replicate every three hours making ~1,000's of mg of magnetite per liter of solution. We have previously demonstrated that this process is scalable (20 ml to > 30 liters) and low cost (~\$10/lb). We are investigating a variety of strains that fall under the thermophilic (high temperature), mesophilic (moderate temperature) and psychrotolerant (low temperature) anaerobic bacteria. Studies have shown that particle size can be somewhat controlled through time and temperature. As an example, thermophilic bacteria (45 to 70°C) generate relatively large particles (30 to 100 nm) at faster rates (1 to 2 days) while psychrotolerant (0 to 37°C) organisms produce smaller particles (10 to 30 nm) at a slower rate (1 to 4 weeks). Furthermore, like chemical co-precipitation, we have demonstrated that the bacteria can synthesize a wide variety of metal substituted magnetite (e.g. Co, Cr, Ni, Pd, Zn, Gd, Mn, Nd).

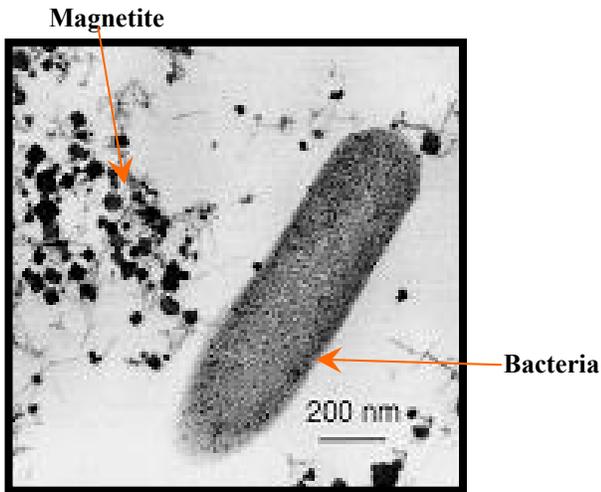


Fig. 4: Bacteria and magnetite

In the following section, we report for the first time on the actual magnetic characteristics of bacterially synthesized magnetic nanoparticles. In particular, we focus on the magnetic characteristics of Zn doped magnetite.

III. PARTICLE CHARACTERIZATION

A detailed analysis of magnetite (Fe_3O_4) nanoparticles shows a size and temperature dependent saturation magnetization. Table 1 provides a summary of some of the

results. Of particular interest is the saturation magnetization of magnetite particles in the 50 nm size range.[27] We will use magnetite in the 50 nm size range as a baseline for comparison.

Table 1: Magnetite magnetization from [27]

Sample	Size (nm)	Temp (°K)	M_s (emu/g)
M5	4	5	56.1
		300	31.8
M10	11.5	5	77.5
		300	60.1
M50	47.7	5	77.8
		300	65.4
M150	150	5	88.5
		300	75.6

Magnetite is based on a spinel structure that contains both octahedral sites and tetrahedral sites where trivalent and divalent ions can occupy, respectively. The magnetic moments of these two sites oppose each other, giving the structure its ferromagnetic qualities. Figure 5 shows this with a Fe^{2+} and a Fe^{3+} in octahedral sites opposing a Fe^{3+} in the tetrahedral site. According to the distribution of cations, there are three types of spinels. In a normal spinel the most common formulation is $A^T[B]_2^O O_4$ where T stands for tetrahedral and O stands for Octahedral. The A ions typically have a 2+ charge and occupy the tetrahedral sites, while the B ions have a 3+ charge and occupy the octahedral sites. This type of distribution takes place in the zinc ferrite: $\text{Zn}^{2+}[\text{Fe}^{3+}\text{Fe}^{3+}]_2\text{O}_4^{2-}$. In an inverse spinel structure the most common formulation is $B^T[A,B]O_4^{2-}$. Half of the B ions occupy tetrahedral sites while the other half occupy octahedral sites. A- ions only occupy octahedral sites. Magnetite, along with NiFe_2O_4 and CoFe_2O_4 , have inverse spinel structure. Introducing transition metal ions into these A- and B- sites provides a wide range of magnetic properties. Not only is it possible to impact saturation magnetization, but it is possible to produce materials that are paramagnetic, ferromagnetic and antiferromagnetic. As an example, Figs. 6 and 7 compare a few samples of metal substituted magnetite. All of the metal substituted samples but one were synthesized bacterially. Table 2 provides the resulting susceptibility and saturation magnetization.

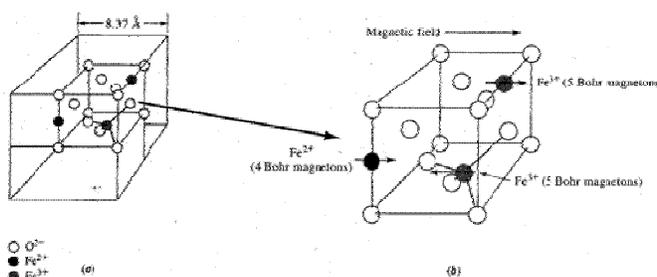


Fig. 5: Magnetite spinel structure[25]

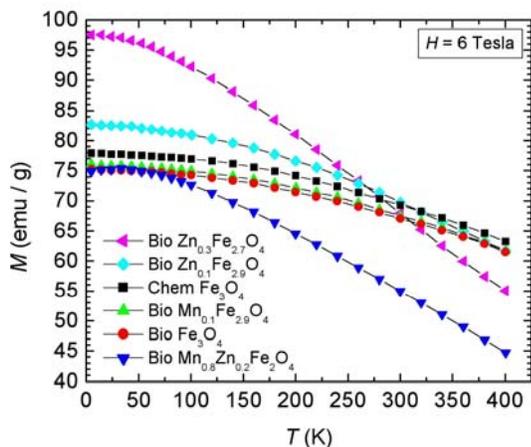


Fig. 6: Comparison of metal substituted magnetite

Table 2: Saturation magnetization and susceptibility measurements of the synthesized samples.

		Susceptibility @ 295K ($\times 10^{-3}$ SI)	Ms @ 5K (emu/g)
Fe ₃ O ₄	Chem	~4.5	77.9
	Bio	~4.5	75.3
Mn	0.1	4	75.9
Zn	0.1	6	82.8
	0.3	8	97.5

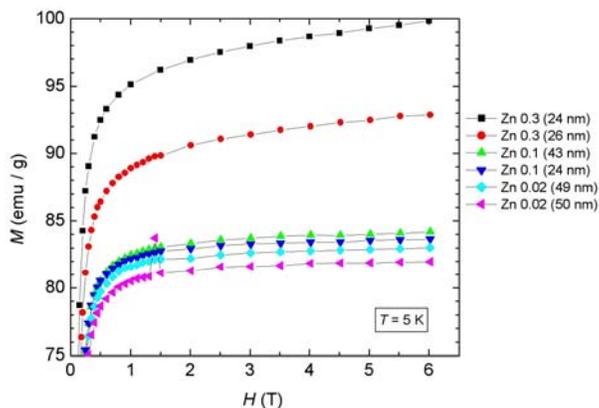


Fig. 7: Magnetization of Bio-synthesized Zn doped magnetite.

The first observation from the figure is the range of magnetization that is a function of doped materials and concentration of doped materials. The chemically synthesized magnetite (Chem Fe_3O_4) serves as a baseline for comparison. The saturation and susceptibility are comparable to levels published in the literature. It is evident that doping impacts both the saturation level and the pyromagnetic (dM/dT) characteristics of the materials. From Fig.6, magnetite has a pyromagnetic coefficient of 0.04 emu/g K. Previous work suggested that the inclusion of Mn and Zn increases the pyromagnetic coefficient (0.093 emu/g K in Fig.6). However, the results in Fig. 6 clearly show that $\text{Zn}_{0.3}\text{Fe}_{2.7}\text{O}_4$ provides the highest sensitivity at 0.123 emu/g K. The saturation level of the biologically synthesized $\text{Zn}_{0.3}\text{Fe}_{2.7}\text{O}_4$ (97.5 emu/g) is noticeably higher than what has been reported in the literature. Nishimura reports a maximum saturation of 83.7 emu/g with a Zn concentration of 0.38.[26] The reason for this discrepancy is still under investigation. However, one possible explanation could be based on the impact of temperature on site selection. All of the conventional approaches to particle synthesis require elevated temperature for the synthesis of the particles. However, since the bacteria act as a catalyst, synthesis of the nanoparticles occurs at a much lower temperature for bacterially synthesized materials in comparison to other methodologies. This lower temperature could encourage a more ordered site selection in the lattice of the nanoparticle which results in higher saturation magnetization. Nakashima et al. suggested that the interaction between magnetic moments on the A- and B-sites is of superexchange type via O^{2-} and results in the magnetic moments being antiparallel to each other.[28] Since the superexchange interaction is stronger for the more closely situated cations, the superexchange interaction of A-O-B (J_{AB}) is the strongest followed by B-O-B (J_{BB}) and A-O-A (J_{AA}). Since zinc is diamagnetic,

introduction of zinc into either the A- or B- site should increase magnetization by elimination of the cancellation due to the antiparallel magnetic moments. Ideally, since the superexchange interaction J_{AB} is the strongest, it would be preferable to locate the Zn^{2+} ion in the B-site. The zinc ion has a preference for the tetrahedral sites in the spinel lattice. By replacing the Fe^{3+} ions in that site, it reduces the amount of opposing magnetic moments in the structure (since it has no magnetic moment) effectively increasing the material's magnetization. Nakashima et al. showed a saturation magnetization for $ZnFe_2O_4$ of 32 emu/g at 300°K. Their synthesis was based on a sputtering method which involved rapid cooling of vapor to form the solid state phase and produces a random distribution of the Zn^{2+} and Fe^{3+} ions in the spinel structure. Figure 7 shows the saturation magnetization of bio-synthesized Zn substituted magnetite. We are presently using neutron scattering to identify which ions are located in the A- and B-sites. If significantly more zinc ions are located in the B-sites, it is possible that the bacteria facilitate particle synthesis results in a lattice configuration that significantly increases saturation magnetization through ordered ion site selection.

IV. CONCLUSION

Magnetic nanoparticles are the building blocks of future magnetic based nanotechnology. First, we describe a novel approach to synthesizing metal substituted magnetite nanoparticles based on thermophilic Fe(III)-reducing bacteria. The primary advantage of such a methodology is high throughput and low cost. We also show that, possibly due to the low temperature environment, the bacterially synthesized materials show a significantly higher magnetization over other synthesis techniques. Other relevant topics presently under investigation include chemical augmentation for fine size control and lower temperature production for smaller particle size.

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