

Mechanism for Sustainable Magnetic Nanoparticles under Ambient Conditions

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(Received 14 July 2007)

Iron-based magnetic fluids are widely used in physical applications. Recently, they have been extended to many biological applications due to their magnetic and biocompatible properties. However, their stability under an ambient environment still has not been systematically investigated. In this report, we present the oxidation process of magnetic fluids. The oxidation process depends on the materials that make the nanoparticles, the diffusion of oxygen atoms from the environment to the magnetic nanoparticles, which mainly depends on the viscosity of the solution and the surfactant that coats the nanoparticles. We suggest three ways to protect nanoparticles from oxidation: (a) using highly viscous carrier liquid (b) using relevant surfactants and (c) substitution of Ni^{2+} and Co^{2+} for Fe^{2+} in magnetite. Methods (a) and (b) are general, so they can be applied for many environmentally sensitive magnetic fluids. Method (c) is specific for a magnetite fluid.

PACS numbers: 75.50.Mm, 87.15.Da, 87.68.+z, 87.83.+a

Keywords: Magnetic fluids, Ferrites, Biophysics, Nanoparticles, Oxidation resistance

I. INTRODUCTION

Magnetic fluids (MFs) have been studied since the 1960s. They are commonly used in many physical applications such as vacuum seals and heat transfer [1]. Recently, the revival of magnetic fluids has attracted much attention because of its many promising applications in biology [2, 3]. Magnetic fluids consist of magnetic nanoparticles (MNPs - that determine magnetic properties of the magnetic fluid), a surfactant (that help MNPs disperse in liquid) and a liquid carrier. Magnetic nanoparticles have the following advantages in bioapplications: (i) small particle size allows particles to attach to biological entities without changing their functions; (ii) large surface area permits strong bonds with surfactant molecules; (iii) their magnetic nature allows them to be controlled by an external magnetic field. Magnetic particles are required to have high saturation magneti-

zation M_s , biocompatibility and stability under working conditions. Fe-based MFs, such as iron ($M_s = 218$ emu/g) or magnetite Fe_3O_4 ($M_s = 90$ emu/g), are potential candidates for bioapplications due to the high value of M_s and their biocompatible. However, they can be oxidized under atmospheric environment, which causes a reduction in M_s with working time. Several papers have reported some surfactants coating MNPs with the ability to protect environment-sensitive nanoparticles [4-6], but the mechanism of oxidation resistance of those MNPs is not clear.

This paper reports a systematic study of the oxidation process and the mechanism by which iron-based MFs can be protected. Fe nanoparticles are sensitive to air, so if we can find a way to protect them from oxidation, that way can be applied to other materials. Fe_3O_4 nanoparticles are the most commonly used in bioapplications. For that reason, we examine Fe and Fe_3O_4 magnetic fluids.

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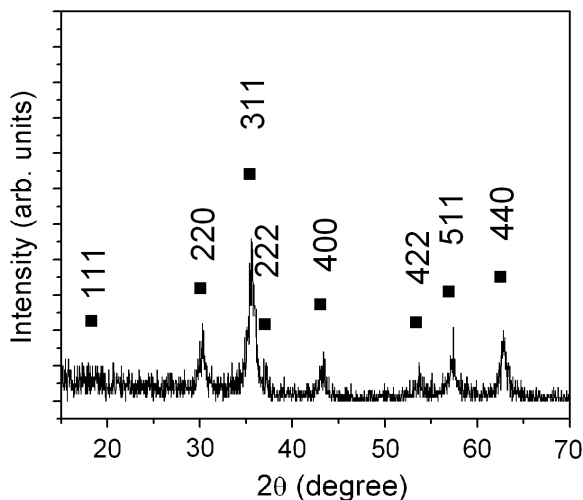


Fig. 1. XRD patterns of a typical sample.

II. EXPERIMENTS

Iron MFs with a particle size of 12 nm are prepared by using the inert-gas condensation technique [7]. Iron atomic vapor is created by sputtering from an iron target under an Ar atmosphere. Fe atoms collide with each other and with Ar atoms to form Fe nanoparticles (NPs). The NPs land on the surface of a rotating drum coated with a mixture of surfactants and low-vapor-pressure oil to have magnetic fluid. The particle size is controlled by changing the sputtering pressure and power. The fluid can be extracted from the vacuum chamber without exposure to air. We use Fe NPs in Octoil and Octoil-S to study the effect of the viscosity of the carrier liquid on the oxidation process of NPs. The samples are exposed in air for a time and mixed before measuring the magnetization at room temperature.

A magnetite fluid with particles with a size of 15 nm are prepared by using conventional coprecipitation of Fe^{3+} and Fe^{2+} ions by OH^- at room temperature. In a typical synthesis, 4.17 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1.52 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (such that $\text{Fe}^{3+}/\text{Fe}^{2+} = 2$) are dissolved in 80 ml of water (concentration of Fe^{2+} is 0.1 M) with vigorous stirring. A solution of 6 ml of 35 % NH_4OH is added at a rate of 1 drop per second at room temperature during constant stirring. Black precipitates of Fe_3O_4 ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) are formed and isolated from the solvent by magnetic decantation. The water washing and the decantation process are repeated four times to remove excess solution. In a similar way, $\text{Fe}_{1-x}\text{Ni}_x\text{O} \cdot \text{Fe}_2\text{O}_3$ and $\text{Fe}_{1-y}\text{Co}_y \cdot \text{Fe}_2\text{O}_3$ nanoparticles with $x = 0.05, 0.1, 0.2, 0.5$ and $y = 0.2, 0.4$ are made by using $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, respectively to replace Fe^{2+} by Ni^{2+} and Co^{2+} . All procedures are conducted under a N_2 atmosphere. To study the oxidation of bare NPs, after washing, we dried the $\text{FeO} \cdot \text{Fe}_2\text{O}_3$, $\text{Fe}_{1-x}\text{Ni}_x\text{O} \cdot \text{Fe}_2\text{O}_3$ and $\text{Fe}_{1-y}\text{Co}_y \cdot \text{Fe}_2\text{O}_3$ nanoparticles and exposed them in

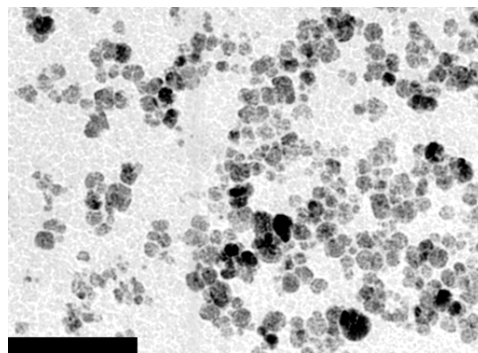


Fig. 2. TEM monograph of a typical magnetite nanoparticle sample. The bar is 100 nm.

air for them to be oxidized; then we measured the magnetic properties. To see the effect of surfactant coating, we vigorously mixed the precipitates in water with polyisobutylene-modified-polysuccinimide (PIB-PS) and then redisperse them in hexane as the carrier liquid. The hexane washing and the decantation are conducted four times to remove excess PIB-PS in the solution. After that, the PIB-PS-coated nanoparticles are dried and exposed in air for them to be oxidized.

The structure analysis of the dried powder of MNPs is conducted by X-ray D5005 diffractometer. The particle size is obtained from a transmission electron microscope (TEM JEM1010-JEOL). The magnetic properties of the iron and the iron oxide are measured by using a Quantum Design MPMS magnetometer and a DMS 880 vibrating sample magnetometer, respectively. Raman spectra are conducted by a Micro Raman T64000 Jobin Yvon system at room temperature. The samples are excited using the 632.8 nm line from a He-Ne laser with a power level of about 1 mW.

III. RESULTS AND DISCUSSION

The structure and the particle size of Fe nanoparticles were presented previously [7]. For the magnetite samples, a typical XRD pattern of unexposed nanoparticles (Figure 1) reveals a magnetite structure (for $x = 0$). This indicates that the particles have an inverted spinel crystalline structure, as in the bulk phase. With the Scherrer formula, a particle size of about 15 nm is calculated for all samples. This value of particle size is in agreement with that obtained from TEM micrographs (Figure 2). The samples after having been exposed in air for 20 days (we think that samples are oxidized to become $\gamma\text{-Fe}_2\text{O}_3$) are subjected to XRD measurements. The XRD patterns of samples before and after exposure to air are similar because the reflection of those two phases are close. When the diffusion process occurs, the oxidation process can be recognized in the Raman spectra. At room temperature, magnetite has a cubic-inverse-spinel structure belonging

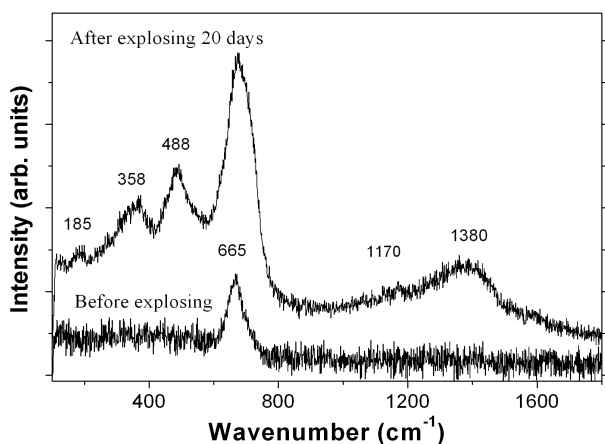


Fig. 3. Raman spectra of Fe_3O_4 nanoparticles before and after exposure in air for 20 days.

to space group $\text{O}_h^7(\text{Fd}3\text{m})$. Group theory predicts the following modes: $\text{A}_g + \text{E}_g + 3\text{T}_{2g}$ are Raman active modes. However, in the case of $\gamma\text{-Fe}_2\text{O}_3$, the Raman spectrum will be related directly to the inverse degree of crystallinity of the materials [8].

Raman spectra of unexposed and exposed powders are shown in Figure 3. In the spectrum of the unexposed sample, there is only one strong peak located at 665 cm^{-1} , which has been assigned to the A_{1g} symmetry mode of the spinel crystalline structure for Fe_3O_4 [9]. The Raman spectrum of a sample after exposure in air for 20 days shows several peaks, 185, 358, 488, 676, 1170 and 1380 cm^{-1} , which are attributed to the $\gamma\text{-Fe}_2\text{O}_3$ phase [10]. The broadened peak over the wavenumbers $600 - 800\text{ cm}^{-1}$ is also a characteristic band of both Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ [11]. The appearance of $\gamma\text{-Fe}_2\text{O}_3$ in the exposed sample indicates that the oxidation process occurs and changes the Fe^{2+} in magnetite $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ to Fe^{3+} . As a result, magnetite $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ ($M_s = 90\text{ emu/g}$) becomes maghemite $\gamma\text{-Fe}_2\text{O}_3$ ($M_s = 60\text{ emu/g}$).

The effect of the viscosity of the carrier liquid is an important factor for oxygen diffusion into the liquid. We study this effect with Fe magnetic fluids with octoil and octoil-s as carrier liquids. Under ambient conditions, the oxidation process of the NPs depends on the diffusion of oxygen from the environment to the particle surface. The diffusive flow of a gas into a liquid is given by

$$J = D \cdot A \cdot \Delta C / \Delta x,$$

where D is the diffusion constant, A is the contact surface area, C is the gas concentration and Δx is the diffusion length. In this formula, D is the factor that is determined by the viscosity of the carrier liquid. The diffusion constant is related to the viscosity η by the Stokes-Einstein equation:

$$D \cdot \eta = kT / 6\pi R,$$

where k is the Boltzmann constant, T is the temperature and R is the radius of the gas atom. A given carrier liquid

has a given viscosity and thus a given diffusion constant, which determines the diffusion time t and the diffusion length x from the surface into the fluid by Fick's law:

$$C(x, t) = \eta \sqrt{4\pi Dt} \exp(-x^2/4Dt).$$

The saturation magnetization of unexposed iron NPs is 87 emu/g . These values are lower than the bulk value, which may be ascribed to the large surface effect and/or possible oxidation during the preparation process. The oxidation process occurs when samples are exposed in air. We measured the M_s of Fe magnetic nanoparticles (no surfactant) in two different carrier liquids: octoil ($\eta = 50\text{ mPa}\cdot\text{s}$) and octoil-s ($\eta = 16\text{ mPa}\cdot\text{s}$). In Figure 3, the oxygen diffusion obtained from Fick's law as a function of the exposure time t in air of Fe nanoparticles in octoil and octoil-s at a certain diffusion length from the contact surface are compared to the decay of the saturation magnetization $M_s(t)/M_s(0)$. The oxidation process, which is recognized by a reduction of $M_s(t)/M_s(0)$, happens with the diffusion process of oxygen into oil. Fe nanoparticles are oxidized almost immediately and completely diffuse without forming a core/shell (iron/iron oxide), as shown in the inset of Figure 3, because of the fact that the shape of the magnetization curves M/M_s did not change after different exposure times (this shape changes with particle size; if they have a core/shell structure, the particle size will reduce and M/M_s will saturate at a higher magnetic field). From these results, we can conclude that a viscous liquid limits oxidation of Fe NPs. By choosing a highly viscous liquid, Fe NPs can be protected.

With the presence of a surfactant, we expect the oxygen diffusion to be limited by the surfactant layer. Surfactant molecules have at least a hydrophobic tail and a hydrophilic head. There are four types of hydrophilic heads: anionic (negative charge), cationic (positive charge), amphoteric (can be negative or positive charge) and nonionic. We have reported the effect of hydrophilic affinity of the head on the diffusion process of oxygen into a Fe magnetic fluid, in which, four surfactants are used: oleic acid (anionic), oleylamine (cationic), oleyl sarcosine (amphoteric) and oleyl ether (nonionic) [12]. The hydrophilic affinity affects the oxidation at a certain level. The saturation magnetization of NPs coated by the surfactants that have chemisorption with a particle surface in the case of oleic acid and oleyl amine reduces slower than that of NPs coated by other surfactants (*i.e.*, oleyl sarcosine and oleyl ether). This indicates that the strong attachment of surfactant molecules to the particle surface has an effect on the oxidation process, but it cannot protect NPs from oxidation. The same effect can be observed in magnetite NPs. Oleic acid cannot protect iron-oxide particles and the magnetite Fe_3O_4 is changed to maghemite $\gamma\text{-Fe}_2\text{O}_3$.

Now we study the effect of the hydrophobic part on the oxidation process. We use polyisobutylene-modified polysuccinimide (PIB-PS) with a molecular weight of 800. Polyisobutylene (PIB) is commonly used to make rubber, which has the best gas isolation ability due to

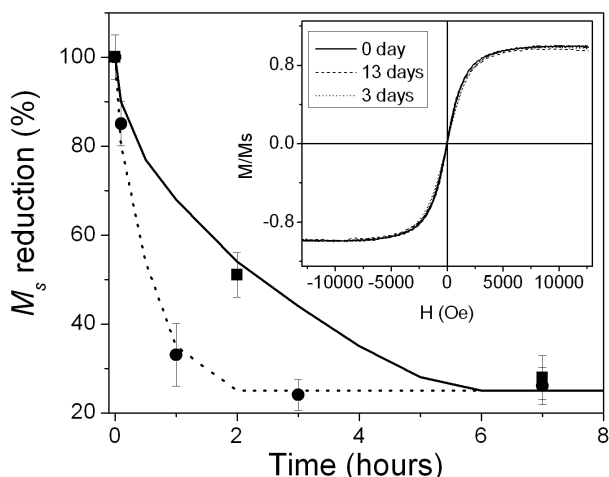


Fig. 4. Experimental (points) $M_s(t)/M_s(0)$ and oxygen diffusion obtained from Fick's law (curves) as a function of the exposure time t in air of Fe nanoparticles in octoil (solid curve) and octoil-s (dotted curve) at a certain diffusion length from the contact surface. The inset is the M/M_s curves of octoil MFs after different exposure times.

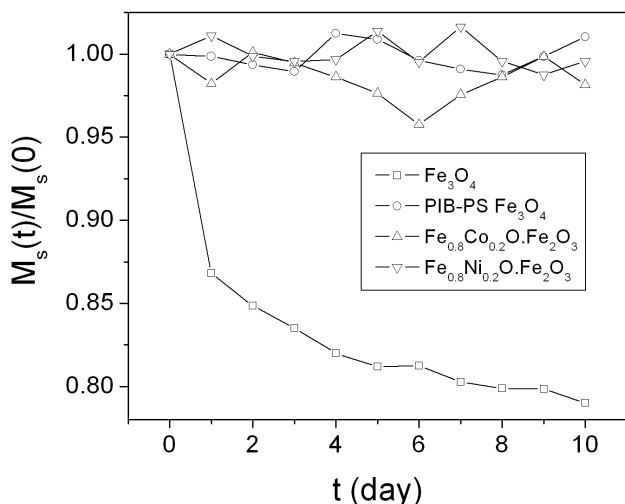


Fig. 5. Saturation magnetization decay as a function of the exposure time of nanoparticles in air.

the saturated and straight hydrocarbon chain. Because of this feature, PIB-PS-coated iron and iron-oxide (Figure 5) MNPs do not show a significant reduction in M_s . PIB creates a thick layer around the particle and prevents oxygen diffusion into the surface. The polymer is modified by polysuccinimide (PS) in the "graft" or "block" way; *i.e.*, the attachment of PIB to the MNP surface is via the PS branch. However, the long PIB branch requires a strong bond to the MNP surface, which can be satisfied by an amine surfactant such as PS. Moreover, PS has amine groups, which are cationic (positively charged due to the possibility of absorption of a proton). On the other hand, the MNP surface is normally negatively charged. In addition, the amine group and the

Table 1. Saturation magnetization M_s and coercivity H_c of $Fe_{1-x}Ni_xO.Fe_2O_3$ and $Fe_{1-y}Co_yO.Fe_2O_3$ ($x = 0.05, 0.1, 0.2, 0.4$ and $y = 0.2, 0.4$) nanoparticles at room temperature. SP stands for superparamagnetic.

N^0	Sample	M_s (emu/g)	H_c (Oe)
1	Fe_3O_4	80	0 (SP)
2	$Fe_3O_4 + PIB-PS$	65	0 (SP)
3	$Fe_{0.8}Co_{0.2}O.Fe_2O_3$	72	60
4	$Fe_{0.6}Co_{0.4}O.Fe_2O_3$	70	115
5	$Fe_{0.95}Ni_{0.05}O.Fe_2O_3$	69	0 (SP)
6	$Fe_{0.9}Ni_{0.1}O.Fe_2O_3$	60	0 (SP)
7	$Fe_{0.8}Ni_{0.2}O.Fe_2O_3$	56	0 (SP)
8	$Fe_{0.6}Ni_{0.4}O.Fe_2O_3$	45	0 (SP)

MNP surface can have a chemisorption ability so that the attachment of an amine surfactant to the MNP is strong enough to bind long hydrocarbon chains of PIB.

The methods to protect NPs from oxidation presented above deal with the environment around the NPs. In many cases, NPs must be dispersed in non-viscous liquid or they must have a specific surface, which cannot be satisfied by surfactants such as PIB-PS. There is another way to overcome this difficulty. It is finding magnetic materials that cannot be changed by the environment. Maghemite, $\gamma-Fe_2O_3$, is a material like that, but the M_s of the bulk form is relatively low, about 60 emu/g, which is much lower for the nanoparticle form. We study magnetite Fe_3O_4 NPs because they are commonly used for bioapplications. For magnetite NPs, we find another way to maintain the high values of M_s , which is substitution of Co^{2+} or Ni^{2+} for Fe^{2+} in magnetite $FeO.Fe_2O_3$. The saturation magnetization and the coercivity of $Fe_{1-x}Ni_xO.Fe_2O_3$ and $Fe_{1-y}Co_y.Fe_2O_3$ ($x = 0.05, 0.1, 0.2, 0.4$ and $y = 0.2, 0.4$) are shown in Table 1. The replacement of Ni^{2+} does not affect the superparamagnetic (SP) behavior of the sample, but the replacement of Co^{2+} changes the SP state to a ferromagnetic behavior by increasing H_c of NPs from almost zero to 60 Oe and to 115 Oe for $y = 0.2$ and 0.4, respectively. The saturation magnetization in both cases reduces with x and y . For a concentration of $x \leq 0.1$, M_s and H_c do not decrease significantly compared to the value for Fe_3O_4 . Figure 5 shows the saturation magnetization decay as a function of the exposure time for bare magnetite NPs, PIB-PS-coated NPs, $Fe_{0.8}Ni_{0.2}O.Fe_2O_3$ and $Fe_{0.8}Co_{0.2}O.Fe_2O_3$. Other compositions of x and y show similar results. The saturation magnetization of the bare NPs is reduced 20 % after 10 days of exposure whereas other nanoparticles show a stability of M_s as the exposure time is increased. The small variation can be explained by errors of measurements. The detailed mechanism for this stability is complicated by the chemical equilibrium of iron-oxides states in the moisture-oxygen-carbon-dioxide system, but we can understand it on the basis of chemical thermodynamics and kinetics. Kinet-

ically, the oxidation of magnetite under exposure conditions involves a topochemical reaction and is influenced by the magnetite crystal size. In small magnetite particles, the diffusion pathways are short and the reaction rates are, therefore, fast so that complete oxidation is achieved rapidly. Replacement of heavy metals such as Co and Ni both reduces the cation diffusion coefficient and increases the activation energy [13,14]. On the other hand, these substitutions change the reduction potentials of the half reactions for oxidation and reduction and result in an oxidation resistance [15]. The samples with $0.05 \leq x \leq 0.20$ are the optimum composition because the samples have oxidation resistance and because the value of M_s is as high as that of the magnetite sample.

IV. CONCLUSIONS

We suggest three ways to protect nanoparticles from oxidation: (a) using a highly viscous carrier liquid, which limits the diffusion of oxygen; (b) using relevant surfactants, PIB-graft-PS and PIB-block-PS; (c) substitution of Ni^{2+} and Co^{2+} for Fe^{2+} in the structure of magnetite. In (b) the hydrophobic tail (PIB) should be a saturated, straight hydrocarbon chain and the hydrophobic head (PS) should be amine group. Methods (a) and (b) are general, so they can be applied for other environment-sensitive magnetic fluids. Method (c) is specific for a magnetite fluid.

ACKNOWLEDGMENTS

This work is financially supported by the Vietnam National Fundamental Research Program for Natural Sciences (406506) and by the European Commission Project Selectnano-TTC.

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