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High magnetization aqueous ferrofluid: A simple one-pot synthesis

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A one-step polyl method was utilized to prepare a stable aqueous iron/iron oxide ferrofluid. The dried powders were characterized by x-ray diffraction, electron microscopy, x-ray absorption spectroscopy, and vibrating sample magnetometry for the determination of phase, morphology, and magnetic properties. To show its potential for imaging applications, the ferrofluid was also investigated as a magnetic resonance imaging contrast agent. © 2010 American Institute of Physics. [doi:10.1063/1.3357342]

Stable colloidal suspensions of magnetic nanoparticles have many appealing qualities that have attracted them to areas of industry, biomedical engineering, physics, and chemistry. Many ferrofluids are used commercially as heat transfer fluids for dampeners in loud speakers, in electronic devices as a form of liquid seals for drive shafts in hard disks, and in medicine as contrast agents for magnetic resonance imaging (MRI) due to their T1 and greater T2 enhancement.1-4 There are two main types of stabilizers for dispersing magnetic nanoparticles such as: surfactant/polymer stabilized nanoparticles and ionically stabilized nanoparticles. These stabilizers allow for the formation of colloidal metal and metal oxide nanoparticles by various types of chemical and physical interactions. For polar solvents, tetramethylammonium hydroxide is commonly used as an ionic stabilizer: the hydroxyl group forms at the nanoparticle surface, providing a negatively charged surface.2 After the synthesis of the nanoparticles, additional precipitation, microemulsion, and aqueous reduction in metal salts.17-23 After the synthesis of the nanoparticles, additional steps are typically required to coat them with the appropriate stabilizer. In most cases, where the goal is an aqueous ferrofluid, the resulting nanoparticle is strictly an iron oxide. This work shows enhanced magnetic properties by forming aqueous stabilized metal/oxide core/shell nanoparticles. The oxide shell forms a passivation layer preventing further oxidation.24

This work presents an alternative method that provides an easier synthetic route and allows for the formation of metal/oxide composite nanoparticles. A modified polyl process is implemented, which allows for more controllable particle morphology along with an overall easier synthetic route. The use of a modified polyl process enabled the liquid polyl to act not only as a solvent but as a mild reducing agent. When coupled with a base, the polyl serves as the perfect medium for reduction in metal salt precursors, while also forming a stabilizing layer on the nanoparticle surface.25-29 This ferrofluid was also investigated in vitro by magnetic resonance relaxivity measurements and in vivo for its application in MRI.

The synthesis of Fe/FeO nanoparticles was carried out under ambient conditions using a modified polyl method. First, two separate solutions were prepared, solution 1 and solution 2. Solution 1 contained 0.25 M iron(II) chloride tetrahydrate and 1.2 propanediol in a 500-ml round bottom flask and was heated to refluxing conditions for 30 min. Solution 2 containing 5.2 M NaOH and 1.2 propanediol was heated simultaneously at 100 ºC with magnetic stirring. Hot solution 2 was subsequently added to solution 1 and heating was continued to refluxing conditions for one hour. The solution underwent a color change from dark orange, gray, and then finally jet black 20 min post addition. After 1 h the solution was allowed to cool to room temperature and then quenched by the addition of methanol. Throughout the reaction the particles did not seem to stick to the magnetic stirrer. The particles were washed with methanol several times and magnetically separated using a rare earth magnet. To prepare an aqueous ferrofluid, the particles were added to a vial with deionized water and sonicated to help the dispersion. The particles are stable in the aqueous media for over one year without visual degradation.

The nanoparticle morphology was confirmed by transmission electron microscopy (TEM) (Fig. 1), which revealed relative size uniformity with an average diameter of 15 (±2.5) nm; the sizes are consistent with dynamic light scattering (DLS) results. X-ray powder diffraction (Fig. 2) shows a mixed phase system with a face centered cubic magnetite

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and a body centered cubic iron. A linear combination fit to x-ray absorption near edge structure (XANES) data determined a composition of 20% metal and 80% oxide, which was also corroborated by Rietveld refinement on the x-ray diffraction (XRD) pattern yielding the same 20/80 ratio. Figure 3 shows the XANES spectra for the ferrofluid material, metallic iron foil and an iron oxide standard. Room temperature vibrating sample magnetometry revealed a saturation magnetization of 100 emu/g (Fig. 4). The saturation magnetization ($M_s$) was obtained from a magnetization versus $1/H$ plot and extrapolating to the point where $1/H$ is equal to zero. The values for bulk Fe and Fe$_3$O$_4$ are 220 emu/g and 80–120 emu/g, respectively. This value in magnetization for nanoparticles containing both iron and iron oxide is expected for the percentages of each component in this mixed phase system.

The nanoparticles also have a surfactant-type coating which will affect the magnetic characteristics of the nanoparticles, as well as act as the colloidal stabilizing agent. Thermal analysis of the dried particles reveals a 20% weight drop that correlates with an organic decomposition at 195 °C. The progressive heating of sodium hydroxide in the polyol not only reduces the Fe$^{2+}$ to produce the nanoparticles but also forms a solution that plays an important role in the overall reaction dynamics. It is hypothesized that a sodium glycolate-type structure or 1,2 propanediol is adsorbed onto the surface of the particles allowing for in situ water stabilization. Further surface characterization will be needed to distinguish between the two possibilities. It is this structure formed around the nanoparticle that gives both the colloidal stability and aids in the resistance to oxidation of the iron metal.

The MRI/spectroscopic experiments were performed on a 2.4 T/40 cm bore MR system (Biospec/Bruker). Spectroscopic $T_1$ and $T_2$ $^1$H relaxation measurements of the aqueous ferrofluid were conducted using an inversion recovery sequence with eight inversion times and repetition times (TR) at least five times the expected $T_1$ value. For the $T_2$ measurements, a multispin-echo CPMG sequence was employed with several echo times and TR values at least five times the expected $T_1$. The relaxation times were computed from least-squares fitting of the exponentially varying signals using analysis routines available at the MR system. Relaxivities were extracted from graphs of relaxation rates ($1/T_1$ and $1/T_2$) versus concentration. The $r_1$ and $r_2$ relaxivities were found to be 8.6 and 382 s$^{-1}$ mM$^{-1}$. These values should be compared to those reported for the commercial contrast agent Feridex, which are 12.3 and 191 s$^{-1}$ mM$^{-1}$.30

The in vivo investigation was performed by intratumoral infusion of the aqueous ferrofluid via convection enhanced delivery31–33 into a tumor bearing rat, 13 days post T9 tumor cell implantation. The aqueous ferrofluid was infused at pH 7.5, an iron concentration of 0.34 mM, and a rate of 0.2 µl/min for a total volume of 18 µL infused. The $T_2$-weighted images in Fig. 5 were acquired during the infusion and up to six days post. The dark contrast due to the ferrofluid is clearly seen in the center of the tumor during the infusion. Then 6 days post infusion, some of the ferrofluid

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The TEM image of magnetite/α-Fe particles prepared by the polyol process in 1,2 propanediol. The TEM shows that the particles size distribution is relatively monodispersed.

FIG. 1. TEM image of magnetite/α-Fe particles prepared by the polyol process in 1,2 propanediol. The TEM shows that the particles size distribution is relatively monodispersed.

FIG. 2. XRD pattern showing a two-phase system of iron oxide and α-iron.

FIG. 3. XANES spectra for the ferrofluid material, and iron foil and iron oxide standards.

FIG. 4. Room temperature vibrating-sample magnetometer data plotted as magnetization (electromagnetic unit per gram) vs applied field (oersted).

FIG. 5. T2-weighted images during the infusion and up to six days post.
has pushed to the periphery, thereby more clearly defining the edge of the tumor.

In conclusion, an aqueous ferrofluid containing monodisperse Fe/FeO nanoparticles were produced using a modified one-pot polyol process. Controlling the reduction in the iron cations, along with the in situ stabilization results in particles with an enhanced magnetic moment over solely iron oxide based ferrofluids due to the incorporation of metallic iron and iron oxide phases in the nanoparticles. These ferrofluids have many promising aspects in biological applications and if linked with a biomolecule, could serve as promising magnetic carriers/labels for efficient bioseparation, drug delivery, and diagnostic applications.

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2S. Odenbach, Ferrofluids (Springer-Verlag, Bremen, Germany, 2002).
3S. Odenbach, Magnetoviscous Effects in Ferrofluids (Springer-Verlag, New York, 2002).
11F. Larach and D. Desvigne, China Particuol. 5, 50 (2007).