Sonochemical Synthesis of Iron Colloids

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Nanostructured materials have been intensively studied in recent years particularly because the physical properties of these materials are quite different from those of the bulk.[1−3] A variety of chemical and physical preparative methods have been developed to produce materials with nanometer domain size, including metal evaporation,[4,5] reduction of metal salts by borohydride derivatives,[6,7] laser pyrolysis,[8] and thermal decomposition.[9] Colloids of ferromagnetic materials are of special interest due to their many important technological applications as ferrofluids.[10,11] Such magnetic fluids find uses in information storage media, magnetic refrigeration, audio reproduction, and magnetic sealing.[12,13] Commercial magnetic fluids are generally produced by exhaustive grinding of magnetite (Fe_3O_4) in ball or vibratory mills for several weeks in the presence of surfactants, which produces a very broad particle size distribution.[10] Chemical methods such as thermolysis of organometallic compounds and metal evaporation have also been applied to produce colloids of ferromagnetic materials.[14,15] We present here a new method for the preparation of stable ferromagnetic colloids of iron using high-intensity ultrasound to sonochemically decompose volatile organometallic compounds. These colloids have narrow size distributions centered at a few nanometers and are found to be superparamagnetic.

Sonochemistry arises from acoustic cavitation, the formation, growth, and implosive collapse of bubbles in a liquid.[16] The collapse of bubbles generates localized hot spots with transient temperatures of $\sim$5000 K and cooling rates in excess of 10^{10} K/s.[17,18] Volatile organometallic compounds inside the cavitating bubble are decomposed to yield individual metal atoms as shown by the observed sonoluminescence from electronic exited states of metal atoms, including Fe.[19] In alkanes, in the

(1) Schmid, G., Ed. *Clusters and Colloids*; VCH Press: New York, 1994.
(2) Weller, H. *Adv. Mater.* **1993**, *5*, 88.
(3) Gleiter, H. *Adv. Mater.* **1992**, *4*, 474.
(4) Hahn, H.; Averback, R. S. *J. Appl. Phys.* **1990**, *67*, 1113.
(5) Klabunde, K. J.; Zhang, D.; Glavee, G. N.; Sorensen, C. M. *Chem. Mater.* **1994**, *6*, 784.
(6) Bönnemann, H.; Brijoux, W.; Brinkmann, R.; Joussen, T. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 273.
(7) Tsai, K.-L. ; Dye, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 1650.
(8) Rice, G. W. In *Laser Chemistry of Organometallics*; Chaiken, J., Ed.; American Chemical Society: Washington, DC, 1993; p 273.
(9) Bradley, J. S.; Hill, E. W.; Klein, C.; Chaudret, B.; Duteil, A. *Chem. Mater.* **1993**, *5*, 254.
(10) Fertman, V. E. *Magnetic Fluids Guidebook: Properties and Applications*; Hemisphere Publishing Co.: New York, 1990.
(11) Berkovsky, B. M.; Medvedev, V. F.; Krakov, M. S. *Magnetic Fluids: Engineering Applications*; Oxford University Press: Oxford, 1993.
(12) Raj, K.; Moskowitz, R. *J. Magn. Magn. Mater.* **1990**, *85*, 233.
(13) Charles, S. W.; Popplewell, J. *IEEE Trans. Magn.* **1980**, *Mag-16*, 172.
(14) Smith, T. W.; Wychick, D. *J. Phys. Chem.* **1980**, *84*, 1621.
(15) Hoon, S. R.; Kilner, M.; Russell, G. J.; Tanner, B. K. *J. Magn. Magn. Mater.* **1983**, *39*, 107.
(16) Suslick, K. S., Ed. *Ultrasound: Its Chemical, Physical, and Biological Effects*; VCH Press: New York, 1988.
(17) Suslick, K. S. *Science* **1990**, *247*, 1439.
(18) Flint, E. B.; Suslick, K. S. *Science* **1991**, *253*, 1397
(19) (a) Suslick, K. S.; Flint, E. B.; Grinstaff, M. W.; Kemper, K. A. *J. Phys. Chem.* **1993**, *97*, 3098. (b) Suslick, K. S.; Choe, S. B.; Cichowlas, A. A.; Grinstaff, M. W. *Nature* **1991**, *353*, 414.
(20) Suslick, K. S.; Hyeon, T.; Fang, M.; Cichowlas, A. A. *Mater. Sci. Eng. A* **1995**, *204*, 186.
(21) (a) Grinstaff, M. W.; Salamon, M. B.; Suslick, K. S. *Phys. Rev. B* **1993**, *48*, 269. (b) Bellissent, R.; Galli, G.; Grinstaff, M. W.; Migliardo, P.; Suslick, K. S. *Phys. Rev. B* **1993**, *48*, 15797. (c) Rozenfeld, O.; Koltypin, Y.; Bamnolker, H.; Margel, S.; Gedanken, A. *Langmuir* **1994**, *11*, 3919.
(22) Suslick, K. S. *MRS Bull.* **1995**, *20*, 29.
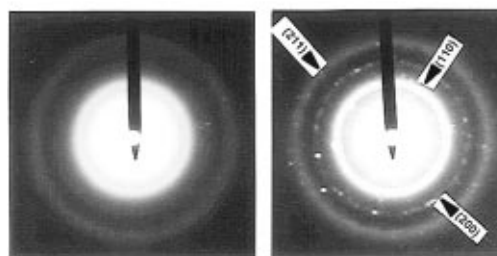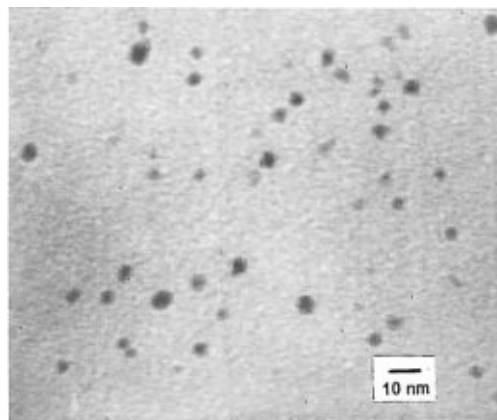(23) Hyeon, T.; Fang, M.; Suslick, K. S. *J. Am. Chem. Soc.* **1996**, *118*, 5492.

Figure 1. (Top) Transmission electron micrograph of sonochemically prepared nanometer iron colloid particles dispersed in a polyvinylpyrrolidone matrix. (Bottom left) Electron microdiffraction pattern before crystallization. (Bottom right) Electron microdiffraction pattern after *in situ* crystallization. Obtained on a Phillips EM400T electron microscope.

absence of any trapping agent, these atoms agglomerate to produce various highly porous nanostructured materials including amorphous metals, alloys, and carbides.[19−23] We have now found it possible to stabilize the nanometer-sized cluster produced during cavitation, preventing their agglomeration and permitting the isolation of stable nanocolloids.

In this work, a volatile organometallic precursor, $Fe(CO)_5$, was sonochemically decomposed in the presence of a stabilizer to create a nanosized iron colloid. Ultrasonic irradiation of 0.2 mL of $Fe(CO)_5$ in 20 mL of octanol with 1 g of polyvinylpyrrolidone (PVP, average molecular weight of 40 000, Sigma Chemicals) at 20 °C under a rigorously oxygen free argon atmosphere produced a black colloidal solution. The TEM (transmission electron microscopy) image in Figure 1 shows that iron particles in the polymer matrix range in size from 3 to 8 nm. Electron microdiffraction shows that these iron clusters are amorphous as initially formed (Figure 1, bottom left). By irradiating the particles with a high-intensity electron beam in the TEM chamber, crystallization was induced presumably from local heating in the electron beam. Electron microdiffraction following the *in situ* crystallization revealed dense ring patterns with d spacings of 2.0, 1.4, and 1.2 Å, which match the standard body centered cubic iron lines (Figure 1, bottom right). Electron microdiffraction also shows a very weak ring pattern with d spacing of 2.5 Å, which corresponds to a slight contamination from the (111) line of cubic iron oxide FeO.

Oleic acid (octadec-9-ene-1-carboxylic acid) can also serve as a colloid stabilizer.[10] The tail of oleic acid is kinked at the double bond, which is critical to its effectiveness: stearic acid, for example, does not stabilize the colloid. A hexadecane solution of 2 M $Fe(CO)_5$ and 0.3 M oleic acid was sonicated at 30 °C for 1 h, during which time the initially yellow solution turned black. The resulting black solution was evacuated at 50 °C for 1 h to remove unreacted iron pentacarbonyl and isolated an inert atmosphere box for further characterization. Transmission electron micrograph revealed that the oleic acid
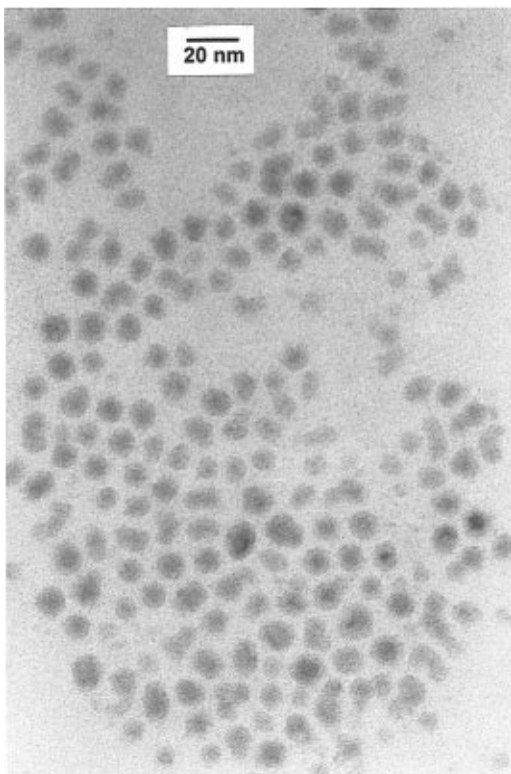
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Figure 2. Transmission electron micrograph of sonochemically prepared iron colloid particles (with average particle size of 8 nm) stabilized by oleic acid.

Figure 3. Magnetization hysteresis loops for the nanometer iron particles dispersed in a PVP matrix at 250 K: (+) magnetization data points; (■) demagnetization points. No hysteresis is observed and consequently the magnetization data points are overlapped by the demagnetization data.

Figure 4. Magnetization (M) versus magnetic field/temperature (H/T) at (■) 200 K, (+) 250 K, and (◇) 290 K, after correcting for the temperature dependence of spontaneous magnetization (I_s/I_o) for the nanometer iron colloid particles dispersed in a polyvinylpyrrolidone matrix.

colloid particles were slightly larger than the PVP colloid but much more uniform, with average particle size of 8 nm (Figure 2). The electron microdiffraction after *in situ* crystallization showed that oleic acid particles are a mixture of Fe and FeO.

When the particles of ferro- or ferrimagnetic materials are smaller than the dimensions of a single domain (which for Fe and Co is ≈20 nm), thermal fluctuations will supersede the Weiss anisotropy above the blocking temperature. Such particles are called superparamagnetic.[24] An operational definition of a superparamagnetism has two requirements. First, the plot of magnetization (M) vs applied magnetic field (H) must show no hysteresis. Second, the magnetization of an isotropic sample at different temperatures must superimpose when plotted against H/T, after correction for the temperature dependence of the spontaneous magnetization. Sonochemically synthesized nanosized iron particles show no hysteresis in their magnetization data at 290 K (Figure 3).[25] Furthermore plots of magnetization vs (magnetic field)/(temperature) for the Fe/PVP sample at 290, 250, and 200 K (Figure 4) superimpose after correction for the temperature dependence of the spontaneous magnetization. Thus, sonochemically prepared nanometer Fe colloids are superparamagnetic.

High saturation magnetization is desirable for magnetic fluid application and is highly sensitive to the method of preparation. The saturated magnetization (M_s) of the initially prepared PVP colloidal nanometer Fe particles is a respectable 101 emu/g (Fe) at 290 K. M_s is determined by extrapolating the experimental plot of M vs $1/H$ using data at high magnetic fields. Standard crystalline bcc Fe has a saturated magnetization of 222 emu/g (Fe) at 298 K,[26] whereas bulk amorphous Fe saturates at 156 emu/g (Fe).[21] The saturation magnetization of our sonochemically prepared iron colloid is greater than that of solvated nanometer-scale iron particles produced by metal vapor deposition (55 emu/g (Fe) at 55 kOe)[27] or ion-exchange resin stabilized nanocrystalline γ-Fe$_2$O$_3$ (99 emu/g at 10 kOe),[28] but smaller than those of copoly(styrene−butadiene)-stabilized iron colloids (120−170 emu/g (Fe) at 10 kOe).[14] For a comparison, the saturation magnetization of a commercial magnetite-based magnetic fluid is 123 emu/g (Fe).[29]

In conclusion, a simple synthetic method has been discovered to produce nanosized iron colloid using high-intensity ultrasound. Nanometer iron particles dispersed in polyvinylpyrrolidone (PVP) matrix or stabilized by adsorption of oleic acid have been synthesized by sonochemical decomposition of Fe(CO)$_5$. Transmission electron micrographs show that the iron particles have a relatively narrow range in size from 3 to 8 nm for polyvinylpyrrolidone, while oleic acid gives an even more uniform distribution at 8 nm. Magnetic measurements revealed that these nanometer iron particles are superparamagnetic with a saturation magnetization of 101 emu/g (Fe) at 290 K. This work is easily extended to colloids of other metals and to alloys of two or more metals, simply by using multiple volatile precursors. For example, we have recently made nanostructured Fe/Co alloys sonochemically.[20] Controlled reaction with O$_2$ or other oxidants will also permit the formation of transition metal oxide colloids.

(24) Jacobs, I. S.; Bean, C. P. In *Magnetism III*; Rado, G. T., Suhl, H., Eds.; Academic Press: New York, 1963; pp 271−351.

(25) Magnetic studies were conducted with a Quantum Design MPMS, 7 T, SQUID magnetometer. Colloidal iron samples were loaded into gelatin capsules inside an inert atmosphere box, carried to the magnetometer under inert atmosphere, and rapidly transferred to the sample chamber. All magnetic data have been corrected for the diamagnetism of the gelatin capsules, solvents, and colloid stabilizers.

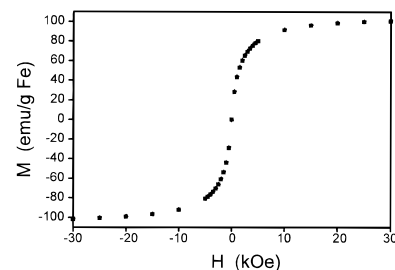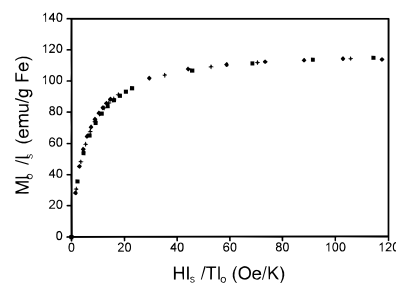(26) Cullity, B. D. *Introduction to Magnetic Materials*; Addison-Wiley: New York, 1972; pp 171−190.

(27) Kernizan, C. F.; Klabunde, K. J.; Sorensen, C. M.; Hadjipanayis, G. C. *Chem. Mater.* **1990**, *2*, 70.

(28) Ziolo, R. F.; Giannelis, E. P.; Weinstein, B. A.; O'Horo, M. P.; Ganguly, B. N.; Mehrotra, V.; Russell, M. W.; Huffman, D. R. *Science* **1992**, *257*, 219.

(29) Ferrofluids Corporation, catalog no. APG 047. Magnetite (Fe$_3$O$_4$) is dispersed in hydrocarbon with an aromatic amine as stabilizer (12.3 wt % of Fe).