

Synthesis and magnetic properties of monodisperse Fe₃O₄ nanoparticles

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We report the high temperature reaction of iron acetylacetonate in phenyl ether in the presence of oleic acid and oleylamine that was used to synthesize monodisperse Fe₃O₄ nanoparticles. X-ray diffraction profile and high-angle annular dark-field images give evidence of self-assembled arrays with nanoparticle size of 4 nm. Magnetization versus temperature in the temperature range 2.5–160 K was measured in zero-field-cooled and field-cooled experiments and a blocking temperature $T_b = 20$ K was obtained. Above T_b the nanoparticles show superparamagnetic behavior and the magnetization versus field for various temperature follows the Langevin function. $M-H$ curves below T_b indicate the ferromagnetic behavior with $H_c = 60-400$ Oe for temperature $T = 2.5-18.5$ K. © 2004 American Institute of Physics. [DOI: 10.1063/1.1682783]

INTRODUCTION

Magnetite or Fe₃O₄ is one of inverse spinel group members with the general formula $A(B)_2O_4$. In Fe₃O₄, the A metal is Fe²⁺ and the B metal is Fe³⁺. The structure of magnetite consists of a fcc closed-packed oxygen arrangement with the divalent Fe²⁺ ion in tetrahedral sites and the trivalent Fe³⁺ ions in octahedral sites. The nanoparticle powder of magnetite has already been synthesized for use as ferrofluid.¹ Also due to their stability and nontoxic property Fe₃O₄ nanoparticles have been investigated for various medical applications.² As an example, if magnetite nanoparticle is coated with proper organic compounds, the resulting material can be dispersed in water and is biocompatible. Due to the interaction of these magnetic nanoparticles with external field they may be guided by appropriate magnetic field to a specific point in body and used as contrast agent in magnetic resonance imaging or for targeted drug delivery.³ Such applications require the nanoparticles to be superparamagnetic. Moreover, the physical properties and, in particular, magnetic properties depend on the size of particles and their distribution. Monodisperse particles are easily managed theoretically since one does not need to include the particle size distribution function such as lognormal in calculations. In this paper we present the synthesis of Fe₃O₄ nanocrystals following the procedure developed by Sun and Zeng⁴ and present a detailed magnetic study of the nanoparticles in a powder form with no substrate. This includes blocking temperature T_b measurements, and superparamagnetic and ferromagnetic properties verification above and below T_b , respectively.

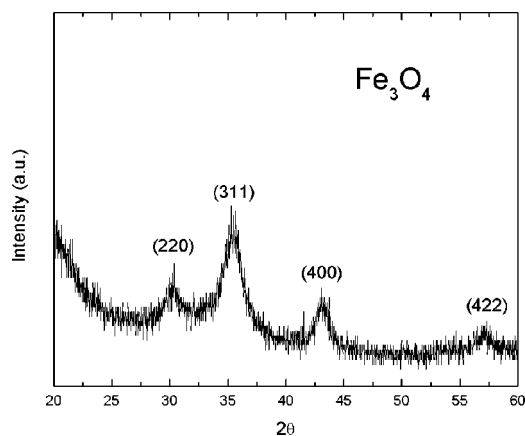
To our knowledge the detailed magnetic characterization of the particles in a powder form synthesized by the method of Sun and Zeng has not been done before. Moreover, the size of the particles (4 nm) is among the smallest reported for

Fe₃O₄ rendering a superparamagnetic material with a very low blocking temperature.⁵⁻⁷ Although the significance of Sun and Zeng method is in its capability to control the particle size and the lattice structure, we have only taken advantage of the small size and have focused on particles in a powder form. The magnetic studies of same nanoparticles dispersed on a substrate with a two-dimensional lattice structure will be discussed elsewhere.

EXPERIMENT

Two millimole of Fe(acac)₃ was mixed in 20 mL of phenyl ether with 10 mmol of 1, 2-hexadecanediol, 6 mmol of oleic acid, and 6 mmol oleylamine. The mixture was kept under nitrogen and was refluxed at 260 °C for 30 min. The mixture was then cooled to room temperature and a dark-brown substance was produced that was treated with ethanol under air. This resulted in the precipitation of a dark-brown particulate material from the solution. The particles were then dissolved in hexane, oleic acid, and oleylamine and reprecipitated with ethanol to give colloidal Fe₃O₄ nanoparticles. The main advantage of this method, also referred to as high temperature polyol reduction, compared to chemical coprecipitation or hydrothermal approach is that the particles are nearly spherical, monodisperse, and the size is easily controlled. Also highly pure phase of Fe₃O₄ crystal is usually prepared.

A JEOL 2010 STEM/TEM analytical electron microscope operating at 200 KV was used to record high-angle annular dark-field (HAADF) images, and the particle composition was determined by energy dispersive x-ray analysis using a Philips model XL-30 scanning electron microscope. X-ray diffraction (XRD) data were obtained on a Rigaku D/MAX-2BX horizontal XRD thin film diffractometer using Cu K_α radiation. The magnetization versus field ($H = 0$ to

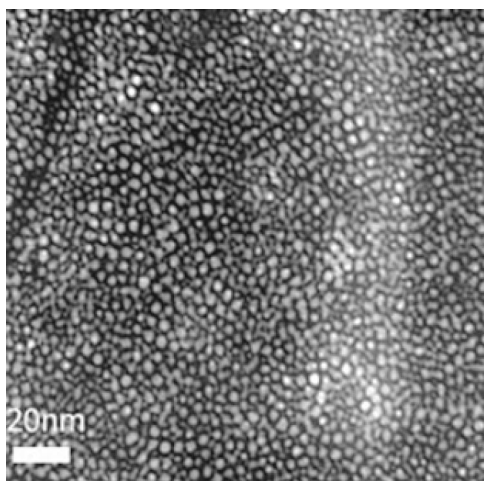
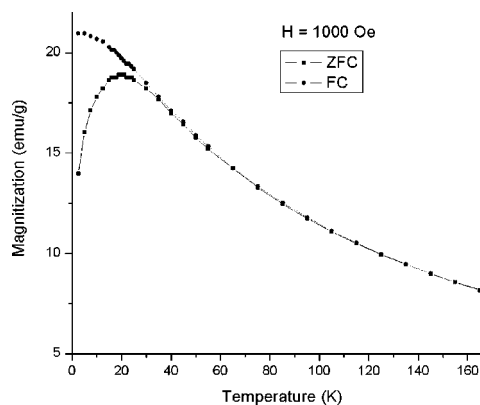
FIG. 1. XRD pattern for as-prepared Fe_3O_4 particles.

± 5 T) and temperature ($T=2.5$ –160 K) were measured using a Lakeshore 4500 vibrating sample magnetometer and a Quantum Design MPMS superconducting quantum interference device magnetometer.

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the nanoparticles displaying all major lines of Fe_3O_4 . The position and relative intensity of XRD peaks of 4 nm Fe_3O_4 nanoparticle is in good agreement with those of the commercial magnetite powder (Aldrich catalog No. 31, 006-9). The HAADF images (Fig. 2) reveal the monodisperse feature of nanoparticles. The average particle diameter of 4 nm estimated from Scherrer formula⁸ from XRD is also consistent with the particle size obtained from HAADF images.

The magnetization versus temperature and field was measured for monodisperse samples in powder form without any substrate. The powder was mixed with low temperature epoxy inside a gel capsule and allowed to dry to immobilize the particles. Magnetic moment versus temperature in the temperature range 2.5–160 K was measured in the zero-field-cooled experiments where the initial field was set to zero as the sample was cooled to the lowest temperature. The

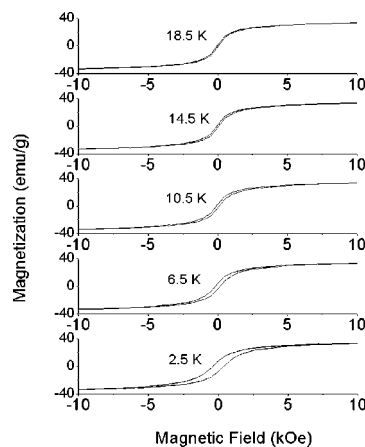
FIG. 2. HAADF image of as-prepared Fe_3O_4 particles.FIG. 3. M vs T for field-cooled (FC) and zero-field-cooled (ZFC) experiments.

field $H=1000$ Oe was then turned on and the magnetic moment versus temperature was measured as the sample was heated from 2.5 to 160 K. In the field-cooled experiments the field $H=1000$ Oe was applied at 160 K and the magnetic moment was measured as the sample was cooled to the lowest temperature of 2.5 K. Figure 3 shows the magnetization versus temperature for these experiments showing a maximum of 20 K for the zero-field-cooled experiment, which is the blocking temperature.

Above blocking temperature the material is superparamagnetic and below that it is ferromagnetic. To verify these features the curves of magnetization versus field were measured at few temperatures above and below blocking temperature. Figure 4 shows M versus field for temperatures below blocking temperature 20 K. The saturation magnetization is about 37 emu/g and coercive field depends on temperature ranging from 60 Oe to 400 Oe for the temperature range 18.5 K–2.5 K, respectively. The data of M versus H/T above T_b for temperatures 30 K–150 K fit to the Langevin function

$$M(H/T) = M_0 [\coth(M_0 m H / k_B T) - (k_B T / M_0 m H)], \quad (1)$$

with M_0 the saturation magnetization, in emu/g, and m the mass of individual particle, in gram. If we consider M_0 and m as fitting parameters, the values $M_0=36.2$ emu/g and m

FIG. 4. M vs H for temperatures below blocking temperature showing the ferromagnetic behavior of the nanoparticles.

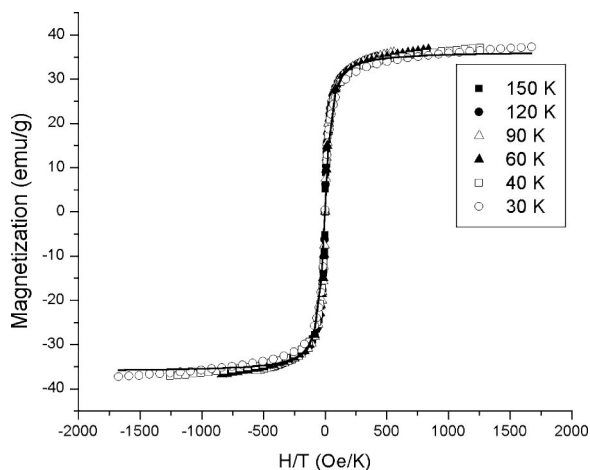


FIG. 5. M vs H/T for temperature 30–150 K with the fitted Langevin function.

$=1.81 \times 10^{-19}$ g are calculated for all temperatures 30–150 K. Taking into account the density of magnetite as 5.046 g/cc, we calculate the diameter of 4.06 nm for the particles, which is in excellent agreement with XRD and TEM results. Figure 5 shows the data of M versus H/T for few temperatures in the range 30–150 K with corresponding fitted curve.

CONCLUSIONS

Monodisperse magnetite (Fe_3O_4) nanoparticles with 4 nm diameter were synthesized using the self-assembly method of Sun and Zeng. XRD profile and HAADF images showed the single phase and lines associated with the inverse

spinel structure and monodisperse feature of the particles. Magnetization measurements on powder samples revealed a blocking temperature of $T_b = 20$ K. Above this temperature the material shows superparamagnetic behavior. From the fit of the magnetization data to Langevin function the particle diameter of 4 nm is obtained, which agrees with the diameter estimated from XRD and HAADF images. The same fit also gives magnetization of 36.2 emu/g for the nanoparticles. Below T_b the nanoparticles are ferromagnetic with coercive field of 400 Oe at 2.5 K and decreasing to zero as the cooling temperature is approached.

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