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Mehdi Zamanpour
Northeastern University

Yajie Chen
Northeastern University

Bolin Hu
Northeastern University

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Authors

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Large-scale synthesis of high moment FeCo nanoparticles using modified polyol synthesis

Mehdi Zamanpour,^{1,3} Yajie Chen,¹ Bolin Hu,^{1,2} Kyler Carroll,⁴ Zachary J. Huba,⁵ E. E. Carpenter,⁵ Laura H. Lewis,² and Vincent G. Harris^{1,2,3,a)}

¹Center for Microwave Magnetic Materials and Integrated Circuits, Northeastern University, Boston, Massachusetts 02115, USA

²Department of Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts 02115, USA

³Department of Chemical Engineering, Northeastern University, Boston, Massachusetts 02115, USA

⁴Department of Nano-Engineering, University of California, San Diego, California 92093, USA

⁵Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia 23284, USA

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Binary alloys of Fe and Co have among the highest magnetizations of any transition metal alloy systems, but their affinity to form oxides act to reduce the magnetization of nanoparticles as their size is reduced below ~ 30 nm. Here, we demonstrate the synthesis of single phase, size-controlled FeCo nanoparticles having magnetization greater than 200 emu/g via a non-aqueous method in which ethylene glycol served as solvent and reducing agent as well as surfactant. Experiments indicated pure-phase FeCo nanoparticles, having saturation magnetization up to 221 emu/g for sizes of 20–30 nm, in single batch processes resulting in > 2 g/batch. Post-synthesis oxidation of nanoparticles was investigated until very stable nanoparticles were realized with constant magnetization over time.

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I. INTRODUCTION

Magnetic nanoparticles (NPs) and their broad range of applications hold great promise in influencing nanotechnologies in areas of catalysis, biomedicine, magnetic resonance imaging, data storage and environmental remediation.¹ Such particles commonly consist of magnetic elements such as iron, nickel and cobalt and their alloys. Several research groups have prepared FeCo-based nanoparticles by different techniques such as thermal decomposition,³ wet chemical processes^{4,5} (aqueous reduction by means of a reducing agent such as borohydride), and chemical vapor deposition.⁶ Desvaux *et al.*⁷ synthesized FeCo nanoparticles of about 150 nm in diameter by thermal decomposition of organometallic precursors under hydrogen and reported magnetization up to 183 emu/g. Chaubey *et al.*⁴ reported obtaining nanoparticles with diameter of 10–20 nm with saturation magnetization of 207 emu/g. Kim *et al.*⁸ also reported the synthesis of 20-nm-diameter particles possessing a saturation magnetization of 206 emu/g by reducing iron and cobalt salts in an aqueous medium. The so-called modified polyol method, in which the solvent is a polyhydric alcohol (polyol) instead of water, is an alternative for the synthesis of magnetic nanoparticles especially those with high tendency to oxidize.

While some groups have used modified polyol method,^{9–11} there is no report on producing high yield batches. Another important issue is oxidation of the particles after synthesis. There is a need to determine the “aging effect” of FeCo nanoparticles.

In this paper, we investigate the large-scale (> 2 g per batch) synthesis of monodispersed, oxide-free FeCo nanoparticles with a high magnetization up to 221 emu/g and the effect of post processing oxidation aging of the magnetic nanoparticles.

II. EXPERIMENTS

A. Synthesis procedure

Stoichiometric quantities of iron chloride, cobalt acetate and sodium hydroxide were mixed and added to ethylene glycol, which served as solvent and surfactant. In all of the experiments we fixed the metal concentration at 0.056 M and 0.014 M for iron and cobalt, respectively. The mixture was stirred and heated, covered with aluminum foil, to a reflux temperature of 200 °C to form nanoparticles. The mixture was cooled to room temperature by removing the heat source and the NPs were separated from the mixture by means of simultaneous magnetic separation and ultrasonication for 1.5 h. After removing the supernatant, the precipitate was rinsed with methanol and centrifuged at 5000 rpm for 15 min several times. Finally, the precipitate was dried in an oven overnight in air at 50 °C.

B. Characterization

The composition of the particles was analyzed by scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX, Zeiss Supra 25), while the morphology of the particles was analyzed by using transmission electron microscopy (TEM, JEOL 2200 FX). The nature of the crystal structure was determined by x-ray diffraction (XRD, Rigaku, Ultima III, CuK $_{\alpha}$ radiation) and the magnetic properties of the

^{a)}Author to whom correspondence should be sent. Electronic mail: vhbb@ece.neu.edu.

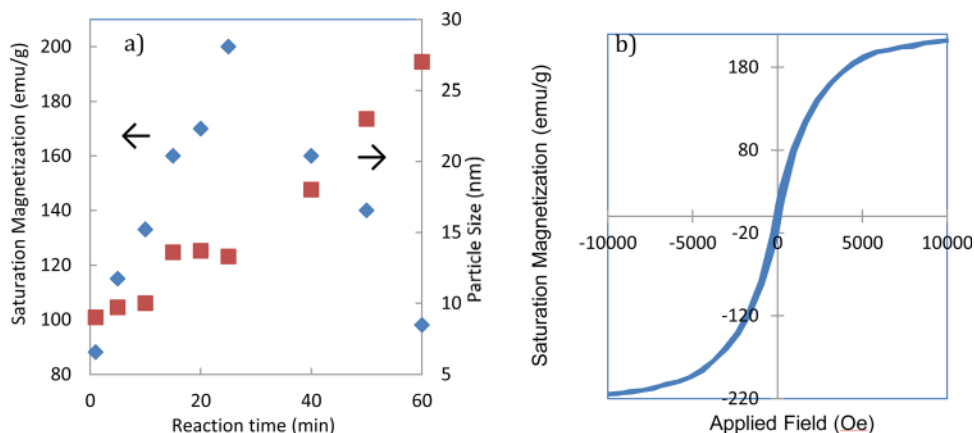


FIG. 1. (Color online) (a) Effect of reaction time on magnetization of the particles and particle size and (b) a hysteresis loop of an oxide-free sample with saturation magnetization of 221 emu/g.

samples were measured at room temperature using a vibrating sample magnetometer (VSM, LakeShore model 7400).

III. RESULTS AND DISCUSSION

Physical properties of the synthesized magnetic nanoparticles, and especially their magnetic moment, are function of the reduction rate of the metals; r . The reduction rate of the metal governs the shape, size and structure of the particles. This reduction rate may be expressed as⁹

$$r = r(P_r, C_{\text{metal}}, C_{\text{OH}}, T, t),$$

where P_r is the reduction potential of the polyol, C_{metal} and C_{OH} are the concentration of metals and hydroxyl ions in the solution, respectively, T is the temperature and t is the reaction duration. A summary of the effects of reaction time and hydroxyl ion concentration on the magnetization of the FeCo NPs is provided below.

A. Effect of reaction time

LaMer describes three steps involved in the growth of mono-dispersed particles in a solution,¹² formation of nuclei, growth of the particles, and growth saturation. Figure 1(a)

shows that reaction times up to 10 min produce NPs with a low room-temperature saturation magnetization indicative of “raw” particles that are largely below the superparamagnetic diameter. After 10 min of reaction time the particles become sufficiently large to exhibit ferromagnetism with high room-temperature saturation magnetization. The trend of increasing magnetization continues to increase with reaction time until $t = 40$ min; at this reaction time the magnetization sharply decreases. This decrease in magnetization at longer reaction times is attributed to the formation of an oxide layer surrounding the particles resulting from a long exposure time to dissolved oxygen in the solution. This is confirmed by XRD spectra (data not shown). Figure 1(b) is a hysteresis loop of a pure-phase sample at room temperature.

B. Effect of salt concentration

Kodama *et al.*¹⁰ hypothesized that hydroxyl ions (OH^-) provide nucleation sites for FeCo nanoparticles during the polyol synthesis. Therefore, (OH^-) concentration plays an important role in the formation and properties of the particles.

Figure 2(a) indicates that a NaOH/(Fe + Co) concentration ratio equal to 12:1 yields particles with an overall low moment that is attributed to insufficient nucleation sites.

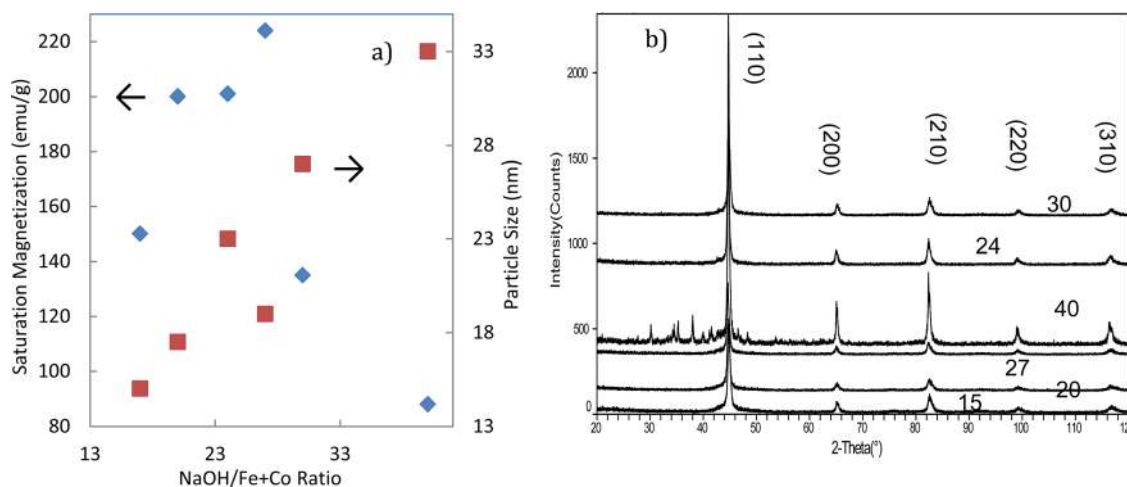


FIG. 2. (Color online) (a) Effect of hydroxyl ion concentration on the magnetization and particle size, and (b) XRD spectra of the samples. (3 lower spectra are at lower concentration in which minor hcp cobalt peaks at 67° and 92° can be seen. The middle spectrum is at the optimized concentration ratio and the upper spectrum is at the high concentration ratio of 40:1. Note also that at high concentration ratio oxide peaks are clearly seen at 30° – 40° . (The numbers on each spectrum indicates the ratio of NaOH/Fe + Co).

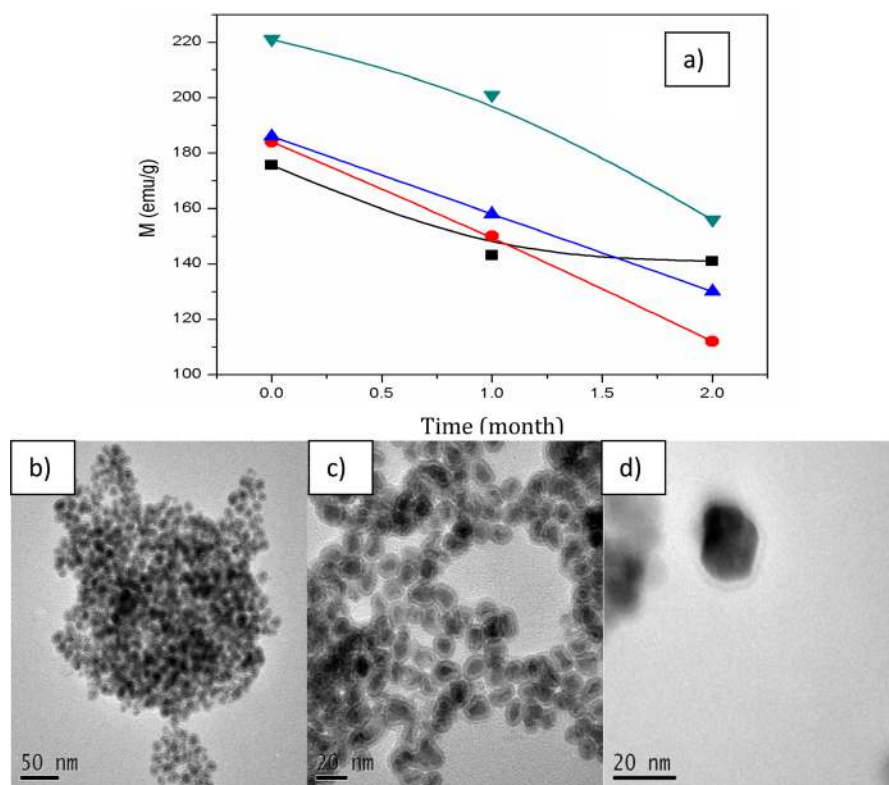


FIG. 3. (Color online) (a) “Aging” of the particles within 2 months and its effect on particles’ magnetization, (b and c) TEM images of clusters of nanoparticles and (d) a single particle. Note the surfactant layer around the particles.

Systematically increasing this ratio to 24:1 yielded nanoparticles with room-temperature saturation magnetization of 221 emu/g. Further increases in the salt: metal ratio beyond 27:1 causes magnetization to decrease sharply to below 200 emu/g likely due to the presence of excessive oxygen in the solution and subsequent oxidation.

C. Effect of aging

Although, we can minimize the adverse effect of oxidation by adjusting the reaction parameters during the polyol synthesis, eventually the particles will be exposed to air somewhere in their applications. To this end, it was desired to determine the effect of “aging” on the nanoparticles by exposing to the air for different times and measured their magnetic properties to determine the extent of oxidation with time. It was noted that the FeCo NPs of this study the aging time takes about 2 months and after that time there is no further significant (less than 2%) decrease in magnetic moment of the particles (Table I and Fig. 3(a)).

After determining the best conditions for the synthesis of high-moment FeCo nanoparticles, the process was scaled to yield 2 g per batch. While a slight decline in the magnetization of the particles was noted (214 emu/g for a 2 g batch versus 221 emu/g for a small (< 0.250 g) batch) the results are sufficiently promising for the purpose of making large batches of magnetic NPs with magnetizations > 200 emu/g.

TABLE I. Decay of saturation magnetization of particles after 2 months.

Sample No.	1	2	3	4
Decay (%)	19	39	30	29

IV. CONCLUSIONS

The synthesis of pure phase FeCo nanoparticles of average diameter of 30 nm with an optimized room-temperature saturation magnetization of 221 emu/g under controlled-size condition was successfully performed. The effects of reaction time and hydroxyl ion concentration in the solution were examined, and the effect of aging on the magnetic properties of the particles was also reported. The synthesis process was scaled to yield 2 g FeCo nanoparticles per batch.

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