

Synthesis and Magnetic Properties of Dendron Capped Fe₂O₃ Nanoparticles

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Using a one-pot reaction technique, monodisperse γ -Fe₂O₃ nanoparticles were prepared by thermal decomposition of Fe(CO)₅ in the presence of a long alkyl chain terminated dendron surfactant. The size of the particles is controlled by adjusting the concentration of the dendron ligands in the reaction solution. Spherical, 2 nm sized nanoparticles were obtained with a 3:1 ratio of dendrons to Fe(CO)₅, while 4.6 nm sized particles were formed with a 1:3 ratio. Superparamagnetic properties of 2 nm, 4 nm, and 4.6 nm sized particles were measured using a SQUID magnetometer.

Key Words : Fe₂O₃, Magnetic nanoparticles, Superparamagnetic, Magnetization measurement, Dendron

Introduction

Magnetic nanoparticles represent a critical link between current technology and future applications due to their unique size dependent properties.¹ Magnetic properties of nano sized materials depend not only on grain size but also size uniformity, crystallinity, and the coating ligand.² Thus, designing synthetic routes to control the size, uniformity, and crystallinity is of particular importance for the application of these magnetic particles.³⁻¹⁰

Anisotropic dipolar interactions of Fe₂O₃ nanoparticles tend to induce aggregation into large clusters, resulting in a loss of specific properties originating from their single domain structure. Numerous synthetic routes using organic surfactant ligands and a polymer matrix for the preparation of size tunable and monodisperse nanoparticles have been reported. Recent reports on the synthesis of magnetic and semiconductor nanoparticles capped by dendrons^{11,12} and a polymer¹³ have demonstrated that these coating molecules are useful in terms of providing direct control over the interparticle distances in magnetic nanoparticle systems.

Application of dendron ligands as a capping material offers many advantages. The steric bulkiness of the dendron ligand provides a closely packed and thick ligand shell over the nanoparticles. Dendron ligands are also ideal for filling the spherical ligand layer, because they can pack naturally in a cone shape on the surface of the nanoparticles. Furthermore, dendron molecules having flexible branches may slow down the possible diffusion of small molecules and ions from a bulk solution to the interface. In this work, we used long alkyl chain terminated organic dendrons with a hydroxyl group at the focal point to obtain iron oxide nanoparticles. These bulky dendron ligands are expected to facilitate the realization of stable nanoparticles with uniform size distribution. Size tuning of the particles was performed by controlling the concentration of the dendrons in the reaction system. These dendron-capped nanoparticles were examined *via* transmission electron microscopy (TEM), a SQUID magnetometer, and X-ray photo electron spectroscopy (XPS).

Experimental

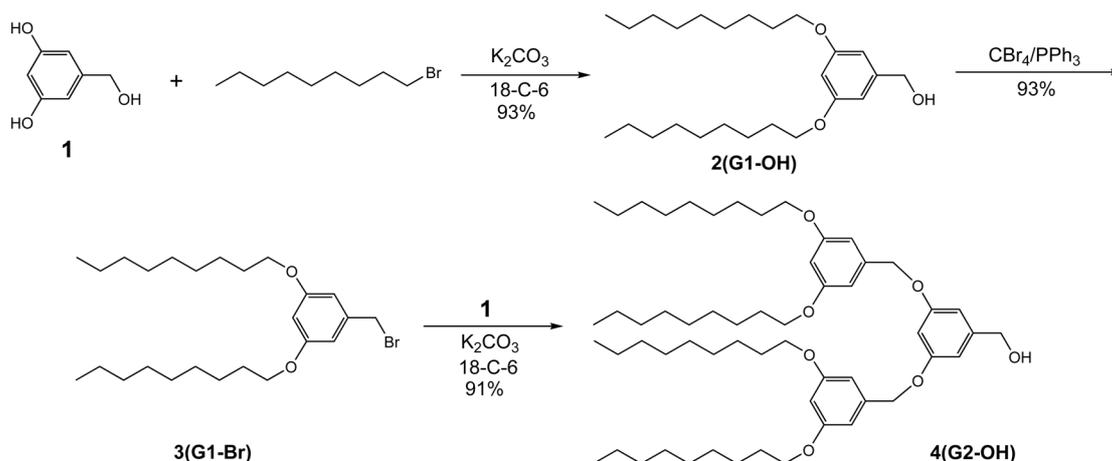
Materials. All syntheses were carried out in standard anaerobic procedures using commercially available reagents. 3,5-dihydroxy benzylalcohol, 1-bromoundecane, carbon tetrabromide, triphenyl phosphine, and crown ether (18-Crown-6) were purchased from Aldrich. *n*-Octyl ether was purchased from TCI and all other solvents used were freshly distilled under anhydrous conditions.

Synthesis of dendron. Alkyl terminated organic dendrons with a hydroxyl group at the focal point was synthesized by modifying the previously reported procedure for benzyl analogue¹⁴ (Scheme 1).

Synthesis of first generation dendron G1-OH. 3,5-dihydroxy benzyl alcohol (dhba) (0.414 g, 3.0 mmol) is refluxed with 1-bromoundecane (1.41 g, 6.0 mmol) in dry acetone in presence of dried K₂CO₃ (1.04 g, 7.5 mmol) and 18-Crown-6 (0.144 g, 0.6 mmol) for 48 hours with vigorous stirring under N₂. Then the mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was partitioned between water and dichloromethane, the aqueous layer extracted with dichloromethane (3 times). The combined organic layers then evaporated to get white solid product. The product was then purified with column chromatography using hexane/EtOAc (7:3) mixture as eluting solvent. R_f 0.63, yield 93%. ¹H NMR (CDCl₃) δ 6.48 (d, 2H), 6.35 (t, 1H), 5.597 (s, 2H), 3.91 (t, 4H), 1.74 (m, 4H), 1.42 (m, 4H), 1.25 (m, 28H), 0.86 (t, 6H).

Synthesis of G1-Br. The G1-OH (0.650 g, 1.45 mmol) and carbon tetrabromide (0.60 g, 1.81 mmol) were dissolved in minimum amount of dry THF and then PPh₃ (0.475 g, 1.81 mmol) was added. After stirring for 20 min under N₂, the reaction mixture was poured into water and extracted with dichloromethane (3 times). The product was further purified by column chromatography using MC as the eluting solvent. Yield 95%; ¹H NMR (CDCl₃) δ 6.5 (d, 2H), 3.37 (t, 1H), 4.40 (s, 2H), 3.92 (t, 4H), 1.76 (m, 4H), 1.44 (m, 4H), 1.268 (m, 28H), 0.88 (t, 6H).

Synthesis of second generation dendron G2-OH. The 3,5-dihydroxy benzyl alcohol (0.137 g, 0.97 mmol) was



Scheme 1. Synthesis of dendron ligand G2-OH.

refluxed with G1-Br (1.00 g, 1.95 mmol) in dry acetone in presence of K_2CO_3 (0.337 g, 2.44 mmol) and 18-C-6 (0.047 g, 0.09 mmol) for 48 hours with vigorous stirring under N_2 . Then the mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was partitioned between water and MC and the aqueous layer extracted with dichloromethane (3 times). The product was further purified with column chromatography using Hexane/EtOAc (7:3) mixture as eluting solvent. (R_f 0.56), yield is 91%; 1H NMR ($CDCl_3$) δ 6.59 (d, 2H), 6.52 (m, 5H), 6.38 (t, 2H), 4.93 (s, 4H), 4.61 (s, 2H), 3.91 (t, 8H) 1.75 (m, 8H), 1.42 (m, 8H), 1.25 (m, 56H), 0.86 (t, 12H).

Synthesis of 2 nm dendron-capped Fe_2O_3 nanoparticle.

Fe_2O_3 nanoparticles were synthesized by modified procedure of Hyeon *et al.*¹⁵ *n*-Octyl ether (10 mL) and G2-OH (4.7 g, 4.56 mmol) was heated to 100 °C under nitrogen atmosphere and constant stirring. $Fe(CO)_5$ (0.2 mL, 1.52 mmol) dissolved in 4 mL *n*-octyl ether was injected to the above solution and kept this reaction mixture at 100 °C for 30 min. The solution was heated upto 250 °C and kept for 30 min. The resulting black solution was cooled to room temperature. The product was precipitated and washed with acetone and dried in vacuum.

Characterization. The size, shape and morphology of nanoparticles were investigated with JEM-2010, Jeol Transmission Electron Microscope. The samples were dispersed in hexane and were dropped and dried over a copper grid. XPS analysis was performed with an ESCALAB-MK (VG Company) instrument. Photoemission was stimulated by a monochromated Al K_{α} radiation (1486.6 eV) with the operating at 12 kV and a 0.10 eV/step interval. Binding energies of spectra were referenced to the C(1s) binding energy set at 284.6 eV. Magnetic measurements were carried out on powder samples using a Quantum Design MPMS XL magnetometer equipped with a 50-kG magnet.

Results and Discussion

Iron pentacarbonyl is a metastable organometallic compound for thermal decomposition that makes it an extremely

useful reagent for producing nano-sized crystals. The standard enthalpy of the formation of iron pentacarbonyl is only $-185 \text{ kcal mol}^{-1}$ and each of the five carbon monoxide subunits have an enthalpy of formation of $-110.5 \text{ kcal mol}^{-1}$, thus accounting for its tendency to dissociate. As illustrated in Figure 1, thermal decomposition of $Fe(CO)_5$ in the presence of a dendron surfactant at high temperature leads to the formation of monodisperse Fe_2O_3 nanoparticles. Maintaining the reaction mixture at 100 °C (just below the decomposition temperature of $Fe(CO)_5$) for half an hour allowed nucleation and growth in a controlled manner, thereby resulting in uniform sized particles. The concentration of the dendron ligands in the reaction solution played a major role in controlling particle size whereas the amount of $Fe(CO)_5$ did not play an important role. Steric bulkiness of the ligand prevents further growth and thus stabilizes the product.

At a high concentration ratio of dendron to $Fe(CO)_5$ (3:1), the smallest particle size, *i.e.*, 2 nm, was obtained while the reversed ratio (1:3) afforded the largest size (~ 4.6 nm) particles. In a reaction ratio of 1:1, 4 nm sized particles were obtained. Thus, the concentration of $Fe(CO)_5$ has only a small effect on the size of the particles, and the size is mostly dependent on the concentration of the dendron ligands. The dendron surfactant is particularly suited to stabilize the nanoparticles since the conical shape of the focal part optimally fits the surface of the spherical nanoparticles and the terminal long chains prevent the small particles from growing. Also, the attachment of the dendron to the surface of the particle serves to increase the inter-particle distance due to its surface coverage ability, and thus minimizes the aggregative tendency of these magnetic particles. This resulted in monodispersed dendron- Fe_2O_3 nanoparticles with a narrow size distribution.

A TEM analysis revealed that the dendron-capped nanoparticles prepared according to the method illustrated in Figure 1 are monodisperse. Figure 2a shows typical TEM images of 2 nm and 4.6 nm particles deposited on a copper grid from hexane dispersions. It can be seen that the particles have a narrow size distribution. The tendency of the particles

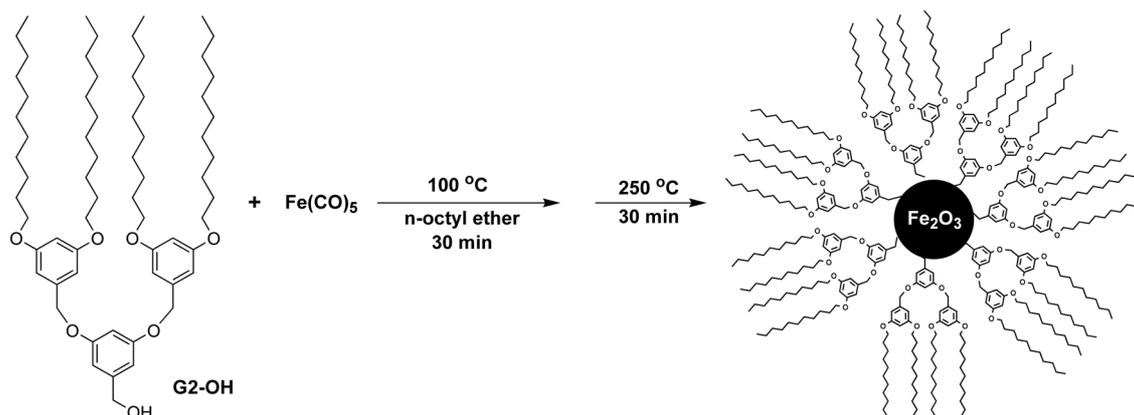


Figure 1. Synthesis of dendron capped Fe₂O₃ nanoparticle.

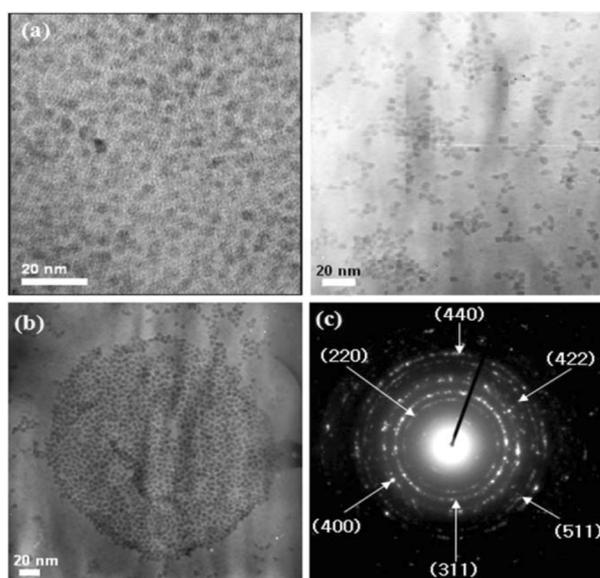


Figure 2. TEM images of dendron capped Fe₂O₃ nanoparticles; (a) (top left) 2 nm, (top right) 4.6 nm. (b) Tendency of the 4.6 nm sized particles to form a self-ordered close-packed lattice at higher concentration. (c) Electron diffraction pattern of 2 nm dendron- γ -Fe₂O₃ particle.

to form a self-ordered close packed lattice²¹ at higher concentration is shown in Figure 2b. The electron diffraction pattern of the material (Figure 2c) verifies the crystalline nature of the dendron capped γ -Fe₂O₃ structures.^{15,17a} The powder XRD analysis failed to obtain any reflections for the sample due to substantial background noise¹⁶ arising from the dendron ligands. In the X-ray photoelectron spectrum (Figure 3), the Fe(2p_{3/2}) and Fe(2p_{1/2}) peaks were located at 711 and 724.25 eV, which are in good agreement with values reported for γ -Fe₂O₃ in the literature.¹⁷

Magnetic studies were conducted on nanoparticles using a superconducting quantum interference device (SQUID). The temperature dependence of magnetization was measured under an applied magnetic field of 100 Oe between 2 and 300 K using zero-field-cooling (ZFC) and field-cooling (FC) procedures. The results shown in Figure 4 are typical for magnetic nanoparticles.^{18,19} The blocking temperature of the

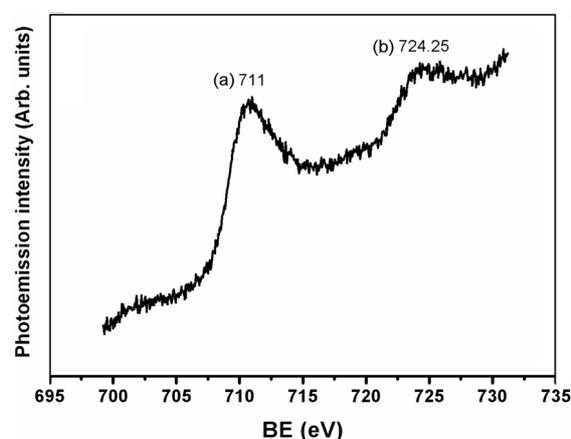


Figure 3. XPS spectra of dendron- γ -Fe₂O₃ nanoparticle; (a) Fe(2p_{3/2}) (b) Fe(2p_{1/2}).

2 nm nanoparticles was found to be lower (10 K) than that of the larger sized (~4 and 4.6 nm) particles (30 and 32 K, respectively). These results are consistent with classical micromagnetic theory wherein it is predicted that the anisotropy energy is proportional to the volume of single particles and the anisotropy constant.^{19,20} Therefore, larger particles

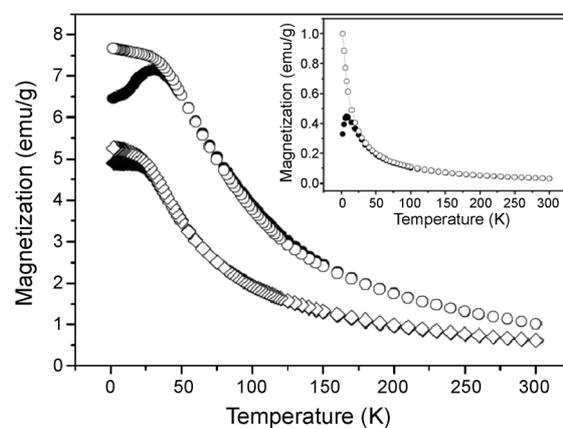


Figure 4. Zero field-cooled and field-cooled magnetization vs. temperature at 100 Oe of 4.6 nm (circles), 4 nm (square) and 2 nm (inset) sized particles.

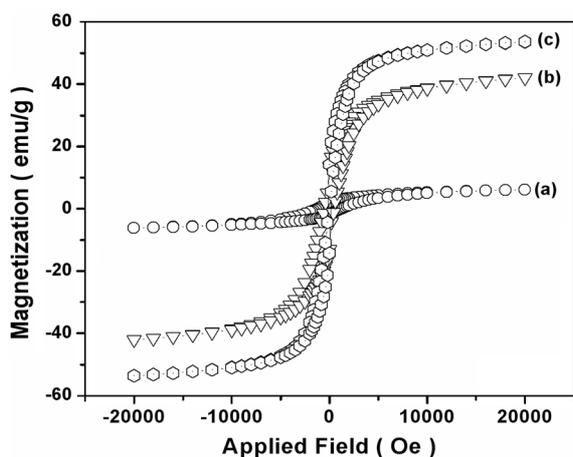


Figure 5. Field dependence of the magnetization at 2 K. Magnetization loops of (a) 2 nm, (b) 4 nm, (c) 4.6 nm sized dendron- γ - Fe_2O_3 nanoparticle.

possess higher anisotropy energy and hence the blocking temperature increases with an increase in particle size.

Magnetic hysteresis measurements of the samples were carried out at 2 K. Figure 5 shows the variation of the coercive field H_c with the size of the particles. The 2 nm sized particles show a high coercivity of 1210 Oe while the 4 nm and 4.6 nm particles gave values of 507 and 125 Oe, respectively. As the particle size increases, the coercivity decreases; this is normal in the case of γ - Fe_2O_3 nanoparticles below blocking temperature T_B . The magnetization (M_s) increases with particle size. The 2 nm particles show the smallest magnetization, about 6 emu/g at 2 tesla, while the 4 nm and 4.6 nm particles show values of 40 and 53 emu/g, respectively. The considerably low value of magnetization for the 2 nm particles is attributed to the presence of a large amount of nonmagnetic component (dendrons) in the sample.

In conclusion, we successfully present a one-pot route to synthesize monodispersed and stable dendron-capped Fe_2O_3 nanocrystals. The size of the nanoparticles was tuned (2–4.6 nm) by adjusting the ratio of dendrons to $\text{Fe}(\text{CO})_5$ with a very narrow size distribution.

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