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Magnetic properties of dendrimer-encapsulated iron nanoparticles containing an average of 55 and 147 atoms†‡§

Marc R. Knecht and Richard M. Crooks*

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The synthesis, characterization and magnetic properties of Fe nanoparticles containing an average of 55 and 147 atoms are described. The nanoparticles are prepared using dendrimer templates, and therefore they are nearly size-monodisperse. In the absence of oxygen and water, the Fe nanoparticles are stable, but they decompose quickly when exposed to air. Magnetic analysis indicates that the 55-atom nanoparticles are superparamagnetic, but the 147-atom materials undergo a transition to ferromagnetic at 6 K. Both materials exhibit suppression of the magnetic saturation compared to bulk Fe.

1. Introduction

Here we report on the synthesis, characterization and magnetic properties of dendrimer-encapsulated nanoparticles (DENs)[1] containing, on average, 55 or 147 Fe atoms. These results are significant for two reasons. Firstly, this study demonstrates that Fe nanoparticles, which are usually easily oxidized, can be prepared in a stable form within dendrimers. Secondly, there are few reported magnetic measurements of Fe nanoparticles in the sub-2 nm size range. We find that DENs composed of 55 Fe atoms (Fe_{55}) are superparamagnetic while Fe_{147} DENs are ferromagnetic at $T < 6$ K. In both cases, the magnetic saturation (M_s) values are suppressed with respect to bulk Fe and depend on the size of the DENs.

Fe nanoparticles are of interest primarily because of their applications in magnetism[2–7] and catalysis.[8–11] For example, metallic Fe nanoparticles are catalysts for environmentally sensitive reactions, including the remediation of Cr^{6+} and Pb^{2+}, and the reduction of carbon tetrachloride and benzoquinone.[8,9] Fe-, as well as Co- and Ni-based materials, also have important magnetic properties.[12] For example, a technological goal is to increase disk storage density by decreasing the size of magnetic domains.[4,13–16] However, small magnetic particles often exhibit superparamagnetism, and their properties are usually highly sensitive to temperature variations. To better understand such effects, there have been numerous studies focused on the development of solution routes to magnetic nanoparticles, particularly Fe.[17,18] These methods have resulted in good protocols for synthesizing nanoparticles having diameters >2.5 nm (~1000 atoms).[6]

Synthetic preparations of Fe nanoparticles rely primarily on two techniques: thermal decomposition[4–7] and the chemical reduction of appropriate precursors.[17,18] For example, the thermal decomposition of $Fe(CO)_5$ in the presence of capping ligands results in Fe nanoparticles having diameters >3 nm.[4–7] It has been found that particle size depends on the synthesis temperature, ligands and other conditions.[4–7] The thermodynamics of nanoparticle nucleation, growth and passivation for the chemical reduction approach are similar to those observed for thermal decomposition, and the resulting particles are similar in size (typically >4 nm). The main difference between the two synthetic procedures arises from the reaction temperature: elevated temperatures are required for thermal decomposition while chemical reduction is usually carried out at room temperature. Chemical reduction is preferred when thermally sensitive stabilizing ligands are employed.[18]

We, and others, have prepared a wide variety of materials using dendrimers as templates.[1,14] The synthetic procedure involves two steps. Firstly, metal ions or complexes are mixed with a solution of poly(amidoamine) (PAMAM) dendrimers. This results in a complex having an average metal ion-to-dendrimer ratio that reflects the original solution concentration of the reactants. Secondly, the metal ion/dendrimer complex is chemically reduced to yield DENs.[1] Because the DEN synthesis is kinetically controlled, and because complexes having particular metal ion-to-dendrimer ratios can be easily prepared, this technique leads to a high degree of size monodispersity. Using this approach, monometallic (Au, Ag, Cu, Pd, Pt and Ni),[14,19–25] bimetallic (alloy and/or core-shell PdPt, PdAu and AuAg)[26–28] and semiconducting (CdS)[29] nanoparticles have been prepared. Iron oxide nanoparticles (diameter = 1–2 nm) have also been prepared using dendrimer templates, but the synthetic approach involves high temperature decomposition of a Fe^{3+}/dendrimer complex rather than chemical reduction.[30] The synthesis is usually carried out in water, but recently we adapted it for organic solvents.[14,24] This makes it possible to exclude water and oxygen from the

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Department of Chemistry and Biochemistry, Texas Materials Institute, Center for Nano- and Molecular Science and Technology, The University of Texas at Austin, 1 University Station, A5300, Austin, TX 78712-0165. E-mail: crooks@cm.utexas.edu; Tel: +1 512-475-8639

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‡ The HTML version of this article has been enhanced with colour images.

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reaction, and thereby prepare nanoparticles from non-noble metals. For example, we previously demonstrated that this approach could be used to synthesize monometallic Ni nanoparticles.[14]

In this paper, we describe the synthesis, characterization and magnetic properties of Fe DENs consisting of an average of 55 and 147 metal atoms. The particles were prepared within sixth generation, amine terminated PAMAM dendrimers modified on their periphery with dodecyl hydrocarbon chains (denoted G6-C_{12}). The resulting DENs had diameters of $\leq$ (1.1 ± 0.2 nm). These materials were characterized using static and time-resolved UV-vis spectroscopy and transmission electron microscopy (TEM), and their magnetic properties were evaluated using a superconducting quantum interference device (SQUID). Magnetic analysis showed that the magnetic saturation of Fe DENs decreased with decreasing particle size. Moreover, Fe_{147} DENs were found to be ferromagnetic below 6 K, while Fe_{55} DENs were superparamagnetic and demonstrated hysteresis-free magnetism at 5 K.

2. Results and discussions

2.1 Synthesis and characterization of Fe DENs

The synthesis of Fe DENs was carried out using hydrophobic dendrimers in dry, oxygen-free toluene to prevent nanoparticle oxidation. The G6-C_{12} template was a sixth-generation PAMAM dendrimer modified on its periphery with 256 dodecyl groups. Complete details about the DEN synthesis are provided in the Experimental section, but a brief summary is provided here. A 2.00 μM solution of G6-C_{12} was prepared in toluene and mixed with sufficient 38.0 mM $FeCl_3$ in THF to yield a metal ion-to-dendrimer ratio of either 55 or 147. This resulted in the formation of a pale yellow solution of the Fe^{3+}/dendrimer composites G6-$C_{12}(Fe^{3+})_{55}$ and G6-$C_{12}(Fe^{3+})_{147}$, respectively. Next, a 10-fold excess of $NaEt_3BH$ (1.00 M in toluene) was added, which led to the formation of a nearly colorless solution. As discussed later, the resulting Fe DENs (G6-$C_{12}(Fe_{55})$ and G6-$C_{12}(Fe_{147})$, respectively) were stable indefinitely under N_2, but precipitated within 5 min after exposure to air.

UV-vis spectra for each step in the synthesis of the Fe DENs are shown in Fig. 1. Addition of 55 equiv. of $FeCl_3$ to the G6-C_{12} solution resulted in the spectrum of G6-$C_{12}(Fe^{3+})_{55}$ shown in Fig. 1a. A 35 nm decrease in λ_{max} was observed for the G6-$C_{12}(Fe^{3+})_{55}$ composite compared to a solution containing only $FeCl_3$ present at the same concentration as used to prepare the dendrimer complex. Similar observations have been reported for Pd and Cu DEN precursors, and are associated with dendrimer encapsulation of the ions.[19,23] Following chemical reduction, the major absorption band of G6-$C_{12}(Fe_{55})$ narrowed and λ_{max} shifted slightly. However, small peak shifts (<10 nm) in this part of the spectrum should be viewed with caution because the solvent (toluene) absorbs in this region and background subtraction is imperfect. Nevertheless, these spectral changes can be attributed to the presence of nanoparticles, and they are consistent with theoretical calculations.[31] The UV-vis spectra for the synthesis of G6-$C_{12}(Fe_{147})$ DENs exhibit similar characteristics (Fig. 1b), but the absorbances associated with the larger particles are higher. Note particularly the higher absorbance at $\lambda > 410$ nm compared to the precursors: this feature is particularly characteristic of zerovalent metallic particles and becomes more apparent with increasing particle size.[25]

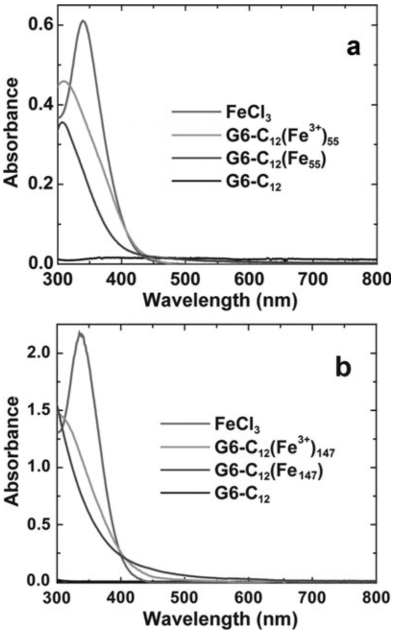

Fig. 1 UV-vis spectra corresponding to the preparation of (a) G6-$C_{12}(Fe_{55})$ and (b) G6-$C_{12}(Fe_{147})$ DENs. Spectra of the starting materials (G6-C_{12} and $FeCl_3$), present at the same concentrations used to prepare the DENs, are also shown.

To confirm the identity of the reduced species, large area energy dispersive spectroscopy (EDS) and kinetically resolved UV-vis spectroscopy were employed. EDS analysis of G6-$C_{12}(Fe_{147})$ DENs dialyzed in the absence of air indicated that the dried particles consisted only of Fe (ESI, Fig. S1†). However, in the solution phase, these materials decomposed when exposed to air. This was demonstrated by monitoring the absorbance at 350 nm as a function of time. During the first hour of the study, the DENs were not exposed to air, and their absorbance did not change. However, as soon as the solution was exposed to air, a dramatic increase in the absorbance occurred, followed by the precipitation of a fine white solid (ESI, Fig. S2†). The absorbance increase can be attributed to light scattering caused by oxygen-induced particle aggregation.[6] This result suggests that the Fe DENs are stable in toluene as long as oxygen is excluded.

TEM micrographs and the corresponding particle size distribution histograms for the Fe DENs are provided in Fig. 2. Analysis of 100 particles indicated particle sizes of 0.9 ± 0.2 nm and 1.1 ± 0.2 nm for the G6-$C_{12}(Fe_{55})$ and G6-$C_{12}(Fe_{147})$ DENs, respectively. These results are comparable to the calculated values of 0.8 and 1.2 nm for Fe particles containing 55 and 147 metal atoms, respectively.[1] A high resolution image of one of the larger G6-$C_{12}(Fe_{147})$ DENs is provided in the Fig. 2c (inset). The high degree of monodispersity is a direct result of the template synthesis.

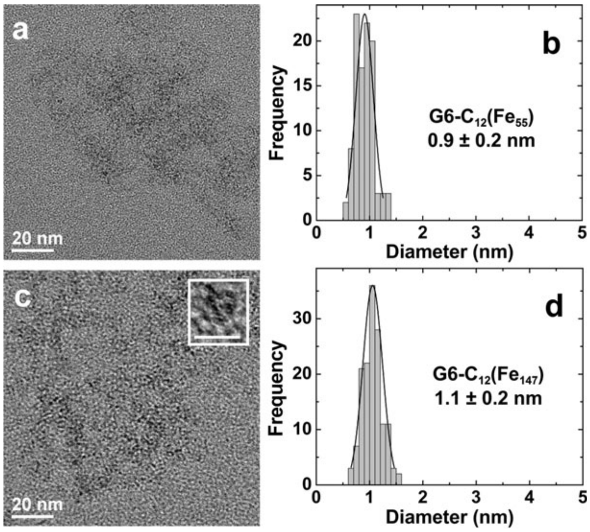

Fig. 2 TEM micrographs and particle size histograms for (a and b) G6-C_{12}(Fe_{55}) and (c and d) G6-C_{12}(Fe_{147}) DENs. The inset in (c) shows a high resolution image of a 1.7 nm Fe_{147} DEN (scale bar = 2 nm).

We attempted additional structural and chemical characterization of the Fe DENs using Mössbauer spectroscopy, X-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (EELS) and powder X-ray diffraction (XRD). However, because of the small size, low *z*-number and other unique structural aspects of DENs, these methods failed to provide useful information. Our lack of success in this regard is consistent with other reports in the literature.[14,30,32,33]

2.2 Magnetic analysis of Fe DENs

Temperature dependent magnetic properties of the Fe DENs were studied using a SQUID magnetometer, having a temperature range of 5 to 300 K (Fig. 3). Both field-cooled (FC) and zero field-cooled (ZFC) analyses were conducted using a magnetic field strength of 500 Oe. For both G6-C_{12}(Fe_{55}) and G6-C_{12}(Fe_{147}), a monotonic increase in the magnetization (M) was observed with decreasing temperature for both the FC and ZFC measurements. This observation is consistent with the effect of temperature on both magnetic pole alignment[34] and our previous observations of magnetic Ni DENs.[14] For G6-C_{12}(Fe_{55}), the ZFC and FC data are superimposable over the temperature range studied. For G6-C_{12}(Fe_{147}), similar results are observed, except that a blocking temperature, T_b, of 6 K is evident in the ZFC data. This indicates that G6-C_{12}(Fe_{147}) DENs are ferromagnetic below 6 K.[35] This value of T_b is comparable to that found previously for 7.0 nm Fe nanoparticles, which exhibited T_b = 35 K at a field strength of 100 Oe.[4]

M–H loops obtained between ±60 kOe at T = 5 K for the Fe DENs are shown in Fig. 4. Importantly, these data are fully reproducible for independently prepared DENs. We have previously shown that the G6-C_{12} dendrimer, and all other reactants present in the sample used to obtain the data in Fig. 4, except for the metallic nanoparticles, are diamagnetic.[14] Therefore, it is clear that the Fe DENs are responsible for the magnetic signals.

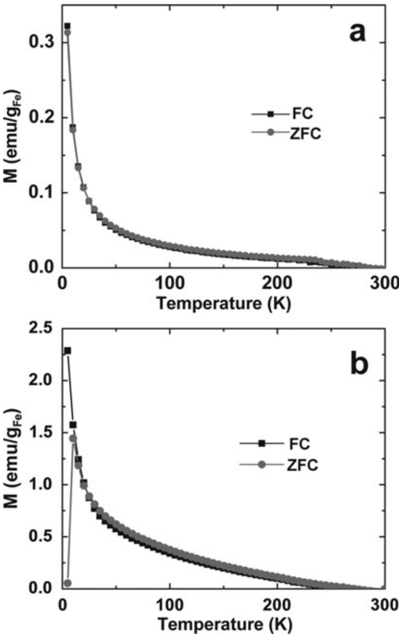

Fig. 3 Plots of magnetization (M) as a function of temperature for (a) G6-C_{12}(Fe_{55}) and (b) G6-C_{12}(Fe_{147}) DENs. The ■ plots correspond to a field-cooled analysis, and the ● plots represent the zero field-cooled analysis. The measurements were made at a field strength of 500 Oe.

Fig. 4a shows the M–H loop for the G6-C_{12}(Fe_{55}) DENs. Here, hysteresis-free magnetism is observed with a M_s value of ~14.0 emu g_{Fe}^{-1}. Complete saturation of the materials was not observed over the range of magnetic fields studied. The absence of hysteresis and a blocking temperature, which

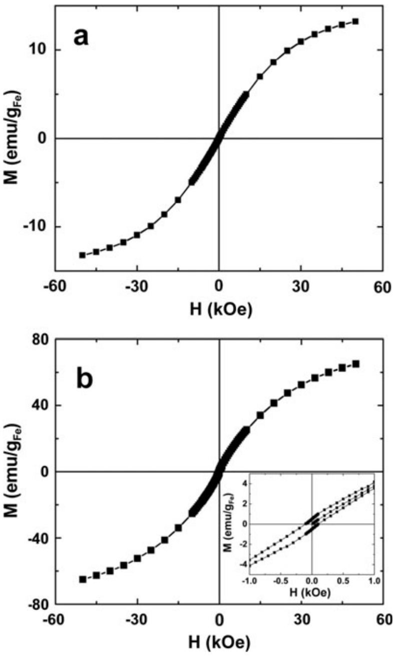

Fig. 4 Magnetization (M) of (a) G6-C_{12}(Fe_{55}) and (b) G6-C_{12}(Fe_{147}) DENs as a function of the applied magnetic field (H) (M–H loops). The inset in part (b) shows the hysteresis associated with the G6-C_{12}(Fe_{147}) DENs.

indicate that the G6-$C_{12}(Fe_{55})$ DENs are superparamagnetic, are a consequence of the small particle size.[35]

Fig. 4b shows the M–H loop for the G6-$C_{12}(Fe_{147})$ DENs. These data were obtained at 5 K (recall T_b = 6 K), and therefore ferromagnetic behavior is observed with an estimated M_s value of 70.0 emu g_{Fe}^{-1} and a coercivity (H_c) of 202 Oe. Note that the M_s value for the G6-$C_{12}(Fe_{147})$ DENs is considerably larger than for the G6-$C_{12}(Fe_{55})$ DENs (~14.0 emu g_{Fe}^{-1}), but that it does not approach the bulk value of 220 emu g_{Fe}^{-1}.[36]

Suppressed magnetization has been observed previously and has been attributed to numerous factors, including surface bond truncation, surface oxidation and the presence of ligands on the surface of the particles.[4,13,14,37,38] DENs are so small that their properties are largely dominated by their surface: about 76 and 63% of the metal atoms in Fe_{55} and Fe_{147} DENs, respectively, reside on the surface. This high degree of incomplete coordination on the surface leads to spin disordering and dominates the suppression of M_s.[13,39] However, secondary effects may also contribute. For example, there could be some oxidation of the nanoparticle surface, but as we have shown previously, it is not possible to use standard methods, such as XPS, to determine if DENs in this size range are partially oxidized.[14] Ligands present on the surface of nanoparticles can also suppress M_s. For example, trioctylphosphine oxide has been shown to suppress M_s values for 4.5 nm Ni particles.[37] However, the effect of ligands on the magnetic properties of Fe nanoparticles are difficult to ascertain because these materials often form surface oxides. This has made it difficult to separate the relative importance of the effects of the ligands and of the oxide.[4,6] Importantly, previous catalysis and EXAFS studies of DENs indicate weak coordination of the dendrimer to the particle surface, and therefore ligand-induced suppression of M_s is probably minimal.[22,40]

3. Experimental section

3.1 Chemicals

Amine-terminated, sixth generation PAMAM dendrimers substituted on the periphery with dodecyl functional groups (G6-C_{12}) were purchased from Dendritech (Midland, MI, USA) as a 10.0 wt% solution in toluene. The vendor specified that 50% of the 512 H atoms on the dendrimer surface were substituted with dodecyl groups. Prior to use, a 200 μM stock solution of G6-C_{12} was prepared in toluene. $FeCl_3$, sodium triethylborohydride and cellulose dialysis sacks (MWCO 12 kDa) were purchased from the Aldrich Chemical Company (Milwaukee, WI, USA). The reductant was received as a 1.00 M solution in toluene. Toluene and THF were purchased from Fisher Chemicals (Pittsburgh, PA, USA). All chemicals were used as received.

3.2 Characterization

UV-vis absorbance spectra were obtained using a Hewlett-Packard HP8453 spectrometer and quartz cuvettes of path length 1.00 cm. Either toluene or THF were used to obtain background spectra, as appropriate. TEM images were obtained using a JEOL-2010F TEM operating at 200 kV. TEM samples were prepared by dropwise addition of the DEN solution onto a carbon-coated Au or Cu grid (EM Sciences, Gibbstown, NJ, USA), followed by solvent evaporation. Magnetic analysis of the particles was performed using a Quantum Design DC-superconducting quantum interference device (DC-SQUID) magnetometer. The mass of metal in each sample was calculated based on the mass of the DEN sample analyzed. These calculations were confirmed by elemental analysis using ICP-MS.[14]

3.3 Preparation of Fe DENs

50 μL of a 200 μM G6-C_{12} stock solution was diluted in toluene to a concentration of 2.00 μM. The dendrimer/metal ion complexes (G6-$C_{12}(Fe^{3+})_{55}$ and G6-$C_{12}(Fe^{3+})_{147}$) were prepared by adding 55 or 147 mol equiv., respectively, of an $FeCl_3$ solution in THF to the dendrimer solution. The final volume of these solutions was 5.00 mL. After bubbling the solutions for 10 min under toluene saturated N_2, 100 μL of a 1.00 M $NaEt_3BH$ solution in toluene was added to complete the synthesis of the Fe DENs. The reduction was allowed to proceed for at least 5 min before the solutions were analyzed.

4. Summary and conclusions

In summary, we have prepared Fe nanoparticles containing an average of 55 and 147 atoms using dendrimeric templates. In the absence of water and oxygen, these DENs are stable indefinitely. A significant result of this study is that a very slight change in particle size, corresponding to less than 100 atoms, results in a transition from superparamagnetic to ferromagnetic behavior at 6 K. This suggests that the DEN templating methodology will be useful for better understanding the magnetic properties of these and other well-defined nanoscale materials.

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