

Synthesis, Characterization, and Magnetic Properties of Dendrimer-Encapsulated Nickel Nanoparticles Containing <150 Atoms

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The synthesis and magnetic properties of Ni nanoparticles containing <150 atoms are described. These materials are prepared in an organic solvent using hydrophobic dendrimers as templates, which results in a high degree of size monodispersity. The dendrimer-encapsulated nanoparticles were characterized by UV–vis spectroscopy, transmission electron microscopy, and energy dispersive spectroscopy. Magnetic (SQUID) studies indicate that the particles are ferromagnetic at 5 K with magnetic saturations that vary depending upon the particle size.

Introduction

Here, we report on the synthesis, characterization, and magnetic properties of Ni dendrimer-encapsulated nanoparticles (DENs)¹ containing <150 atoms. These new results are significant for two reasons. First, DENs prepared from an easily oxidizable metal like Ni have not previously been reported. Thus, the synthetic approach reported here provides a means for preparing a vast range of new nanomaterials having well-defined structures, compositions, and sizes that are difficult or impossible to prepare using alternative approaches. Second, the magnetic properties of zerovalent Ni nanoparticles in the <3.0 nm size range have not previously been measured. We find that Ni DENs are ferromagnetic with minimal hysteresis at low temperatures (5.0 K) due to their small diameters (<1.4 nm) and high degree of size monodispersity. Magnetic data for 1–3 nm monometallic and multimetallic nanoparticles of this type are scarce, and therefore a significant outcome of the present study is that the DEN templating method provides a means for better understanding the magnetic properties of such materials.

Magnetic nanomaterials, particularly those based upon Fe, Co, and Ni, have been intensively studied to develop a better understanding of their fundamental properties and also because of their potentially important technological applications. The latter include magnetic storage,² catalysis,^{3–5}

remediation of toxins,^{6–8} biological imaging,⁹ and magnetotaxis.¹⁰ However, synthetic approaches for preparing well-defined materials in the <5 nm size range are limited. For example, the smallest zerovalent Fe nanoparticles that have been prepared have sizes >2.0 nm.^{8,11–13} Cobalt nanoparticles having diameters as small as 2.5 nm have been prepared using inorganic and organometallic precursors,^{14,15} and Co clusters having diameters of 0.8 nm have been prepared within the interior of crystalline molecular sieves.¹⁶

Ni nanomaterials are of interest because of their catalytic and magnetic properties.^{4,17} Because these properties can be tuned by manipulating the size and structure of the particles, the development of flexible and precise synthetic routes has been an active area of research.^{18–22} At present, Ni nano-

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particles are generally prepared by microemulsion techniques, using cetyltrimethylammonium bromide (CTAB),¹⁸ or by reduction of Ni ions in the presence of an appropriate ligand,^{18–20} such as alkyl amines or trioctylphosphine oxide (TOPO).²² The surfactants passivate the surface of the nascent Ni nanoparticles, and thereby retard growth and prevent agglomeration. These methods have been used to prepare zerovalent Ni particles having diameters of >4.0 nm and dispersities ranging from 6% to 20%.¹⁹ For example, Hyeon and co-workers recently prepared ligand-passivated, Ni-containing nanoparticles having sizes ranging from 2 to 13 nm.^{23,24} When first synthesized, the larger particles consisted primarily of zerovalent Ni, but these converted to NiO within 24 h. Only the presence of NiO was detected for particles <5 nm in diameter.²³ Other synthetic methods, based on laser decomposition of metal precursors, have also been reported.^{25,26} For example, aerosols containing Ni²⁺ decompose to yield zerovalent Ni nanoparticles having diameters >12 nm.²⁵ Following gas-phase synthesis, these materials were stabilized in toluene solutions of oleyl-amine or oleic acid, which most likely binds to the particle surface. At present, however, there are no reports in the literature of solution-phase routes to zerovalent Ni nanoparticles having diameters of <4 nm.

The physical properties of materials exhibit dramatic changes as their size is reduced below 10 nm, and these effects are particularly pronounced for particles having diameters of <3 nm. For example, Au nanoparticles have been shown to undergo a continuous change in electrical properties from bulk-like to molecule-like over the size range of 3 to 1 nm, respectively.^{27,28} Similar observations have been made for the relationship between the size of Ni nanoparticles and their catalytic properties.^{29,30} However, until now it has not been possible to synthesize zerovalent Ni nanoparticles having diameters of <4 nm via solution routes, and therefore the effect of size on magnetic properties in this most interesting size range has not been carefully examined. Specifically, the smallest zerovalent Ni nanoparticles thus far characterized by magnetic methods were around 4 nm in diameter¹⁸ and thus contained about 4200 atoms, while here we focus on particles containing 55 and 147 atoms. Note that gas-phase techniques have been used to produce small

Ni clusters (<1.0 nm), but that the magnetic results for similarly sized clusters prepared by different procedures produced different results.^{31,32} For clusters prepared in the gas phase, an enhancement in the magnetism was observed with diminishing cluster sizes,³¹ while the opposite trend of decreasing magnetism with decreasing particle sizes resulted from particles prepared via ion implantation within AlN.³²

Dendrimers have been used as templates for the synthesis of metallic (Au, Ag, Cu, Pd, and Pt), bimetallic (AuAg, AuPd, PdPt, PtAu, and PdRh), and semiconducting (CdS) nanoparticles.^{1,33} DENs are synthesized by mixing solutions containing dendrimers and metal ions. This results in extraction of the metal ions into the dendrimer interior, and subsequent chemical reduction of this composite results in formation of DENs. This type of synthesis is kinetically controlled, and therefore it does not result in the broad size distributions associated with the thermodynamics of nucleation and growth.³⁴ Instead, the size of DENs is controlled by the metal-ion-to-dendrimer ratio and the dendrimer generation. The synthesis of DENs is normally carried out in water,¹ but recently we reported an approach that permits them to be prepared in nonpolar, organic solvents.³⁵ DENs usually have diameters <3.0 nm and a high degree of size monodispersity (± 0.3 nm). One final point: the surfaces of DENs are only partially passivated,^{28,36–38} and therefore they are catalytically active and ligand effects on their magnetic properties are expected to be minimal.

In this paper, we describe the synthesis and magnetic properties of Ni DENs containing 55 and 147 metal atoms. The Ni nanoparticles reported here were prepared within sixth-generation poly(amidoamine) (PAMAM) dendrimer templates functionalized on their periphery with alkyl groups. This renders them soluble in toluene and thus protects them from oxidation by water and oxygen. Ni DENs having diameters of $<(1.5 \pm 0.3)$ nm were characterized using UV–vis spectroscopy, transmission electron microscopy (TEM), and single-particle energy dispersive spectroscopy (EDS) and using a superconducting quantum interference device (SQUID) for magnetic analysis. The results indicate that the synthesis yields magnetic Ni DENs that have a size-dependent magnetic saturation and minimal coercivity.

Experimental Section

Chemicals. Amine-terminated, sixth-generation PAMAM dendrimers substituted on the periphery with dodecyl functional groups (G6-C₁₂) were purchased from Dendritech (Midland, MI) as a 10.0

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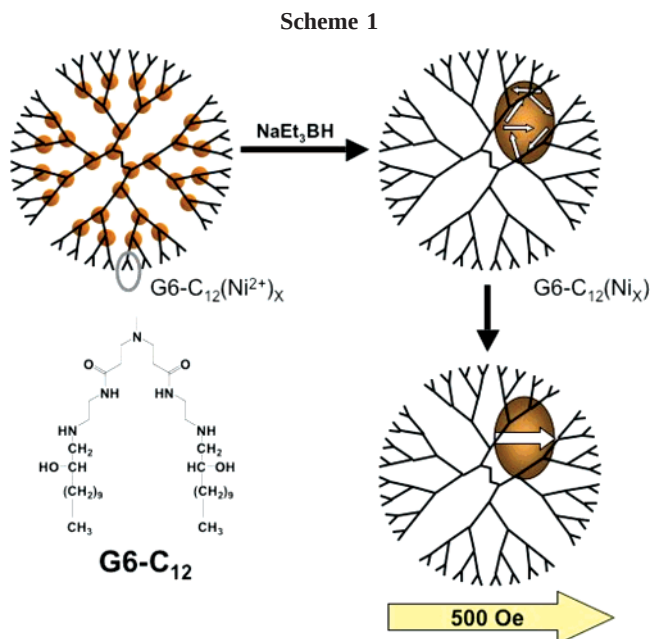
wt % solution in toluene. The manufacturer indicates that 50% of the 512 H atoms on the surface of the dendrimer are substituted by dodecyl groups. Prior to use, a 200 μM stock solution of G6-C₁₂ was prepared in toluene. Ni(ClO₄)₂·6H₂O was purchased from the G. Frederick Smith Chemical Company (Columbus, OH), while sodium triethylborohydride was purchased from the Aldrich Chemical Co. (Milwaukee, WI) as a 1.00 M solution in toluene. Toluene and THF were purchased from Fisher Chemicals (Pittsburgh, PA) and used as-received.

Characterization. UV–vis absorbance spectra were obtained using a Hewlett-Packard HP8453 spectrometer and quartz cuvettes having a path length of 1.00 cm. As appropriate, either toluene or THF was used to obtain background spectra. TEM images were obtained using a JEOL-2010F TEM operating at 200 kV. Samples were prepared by dropwise addition of the sample onto a carbon-coated Au grid (EM Sciences, Gibbstown, NJ) followed by solvent evaporation. Single-particle EDS was conducted using an INCA-EnergyTEM EDS System with a 30.0 mm² Li drifted detector. Spectra of individual particles were obtained using a 1.00 nm beam diameter and an acquisition time of 20.0 s. Magnetic analysis of the particles was performed using a Quantum Design DC-superconducting quantum interference device (DC-SQUID) magnetometer. The mass of Ni 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.

Preparation of Ni DENs. Fifty microliters of a 200 μM G6-C₁₂ stock solution was diluted in toluene to a concentration of 2.00 μM . The dendrimer/metal-ion complexes (G6-C₁₂(Ni²⁺)₅₅ and G6-C₁₂(Ni²⁺)₁₄₇) were prepared by adding 55 or 147 mol equiv, respectively, of a Ni(ClO₄)₂·6H₂O solution in THF to the dendrimer solution. Caution was used when handling solutions of Ni complexes as they are suspected cancer agents. The final volume of these solutions was 5.00 mL. After the solutions were bubbled for 10 min under toluene-saturated N₂, 100 μL of a 1.00 M NaEt₃BH solution in toluene was added to complete the synthesis of the Ni DENs (G6-C₁₂(Ni₅₅) and G6-C₁₂(Ni₁₄₇), respectively). The reduction was allowed to proceed for at least 5 min before the solutions were analyzed.

Results and Discussions

Synthesis and Characterization of Ni DENs. The Ni nanoparticles reported here were prepared within dendrimer templates functionalized on their periphery with alkyl groups to render them soluble in toluene. This makes it possible to exclude water and oxygen from the Ni surface. Ni nanoparticles containing an average of 55 or 147 atoms were prepared within G6-C₁₂ templates using an approach we previously described for the synthesis of Au DENs (Scheme 1).³⁵ First, appropriate stoichiometric ratios of Ni(ClO₄)₂·6H₂O were added to 2.00 μM solutions of G6-C₁₂ with vigorous stirring. The resulting dendrimer/metal-ion complexes are denoted as G6-C₁₂(Ni²⁺)_x ($x = 55$ or 147). Second, a 10-fold excess of sodium triethylborohydride (in toluene) was added to reduce the dendrimer–metal complexes to the analogous zerovalent DENs. Upon reduction, the solution changed from colorless to a golden-brown color, which is characteristic of metal nanoparticles.¹⁷ There was no evidence of precipitation and if kept under nitrogen the solutions were stable indefinitely. However, when exposed to air, the color faded, followed by precipitation of a fine white solid. We used time-resolved UV–vis spectroscopy to better understand this observation. The experiment was carried out as



follows (Supporting Information, Figure S1). First, a Ni DEN solution was prepared and maintained under a N₂ atmosphere: no change in the UV–vis spectrum was observed as a function of time. Next, the solution was exposed to air, and immediately the color of the solution began to fade. Within 5 min the absorbance characteristic of Ni DENs was lost entirely. This observation is consistent with a change in oxidation state of the DENs from 0 to 2+, that is, air oxidation of Ni DENs to NiO. Note that bulk Ni precipitates from solution immediately when the reduction of Ni²⁺ is carried out in the absence of the dendrimer template.

Figure 1 provides UV–vis spectra obtained during each step of the Ni DEN synthesis as well as spectra of the starting materials (present at the same concentrations as G6-C₁₂–(Ni²⁺)_x and G6-C₁₂(Ni_x)). The starting materials (G6-C₁₂ and Ni(ClO₄)₂·6H₂O) have very low absorbances at the concentrations used for the DEN syntheses (note that below 280 nm there is a strong absorbance due to toluene). Spectra of the dendrimer/metal-ion complexes (G6-C₁₂(Ni²⁺)_x) are also featureless. However, following reduction, the Ni DENs exhibit an increase in absorbance toward lower wavelengths, which is consistent with previous spectroscopic results for other types of metal particles in this size range.^{39,40} Also consistent with previous studies, we find that the absorbance of the larger Ni particles (part b of Figure 1) is higher throughout the wavelength range studied compared to that of the smaller particles (part a of Figure 1).^{41,42}

Figure 2 provides representative TEM micrographs and the corresponding size-distribution histograms for Ni₅₅ and Ni₁₄₇ DENs. Analysis of more than 100 randomly selected particles revealed an average diameter of 0.8 ± 0.2 nm for

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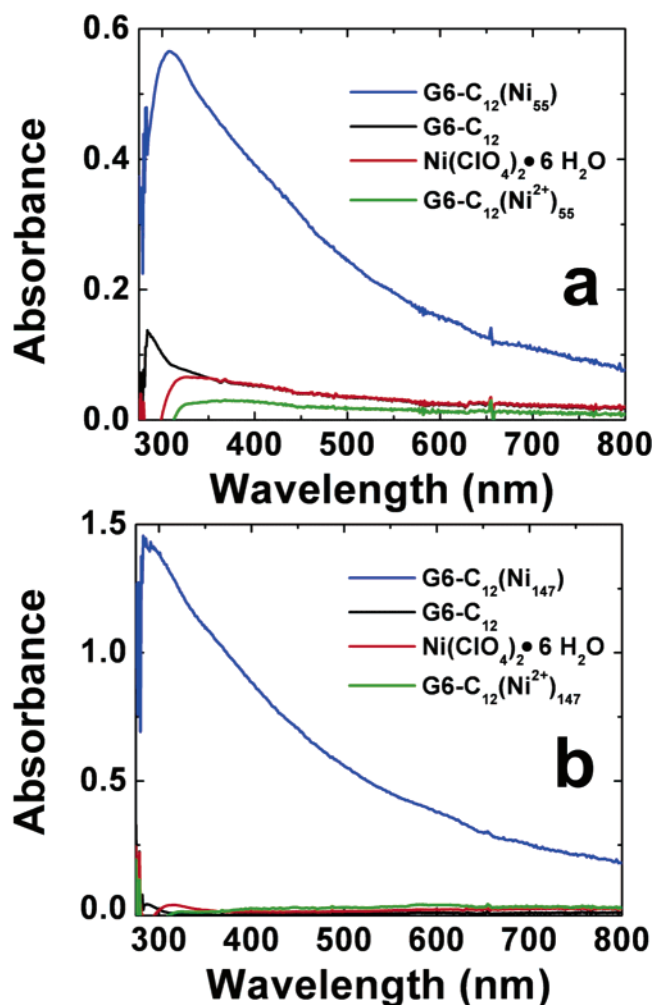


Figure 1. UV-vis spectra of (a) G6-C₁₂(Ni²⁺)₅₅ and (b) G6-C₁₂(Ni²⁺)₁₄₇ before and after reduction. Spectra of the dendrimer only and Ni(ClO₄)₂·6H₂O only ([Ni(ClO₄)₂·6H₂O] = 110 μ M for (a) and 294 μ M for (b)) are also shown. The dendrimer concentration was 2.00 μ M in all cases. The negative-going absorptions in (a) are due to imperfect subtraction of the toluene background, which absorbs strongly at $\lambda < 280$ nm.

Ni₅₅ and 1.2 ± 0.3 nm for Ni₁₄₇. Both experimental results are comparable to the calculated diameters of 1.0 and 1.2 nm.^{1,43} The agreement between the measured and calculated diameters, as well as the high degree of monodispersity, are a direct consequence of the template-based synthesis.¹

Single-particle EDS analysis was used to confirm the elemental identity of the nanoparticles (Supporting Information, Figure S2). Analysis of individual particles yielded peaks corresponding to Ni, Au, Na, and Cl. The latter three elements arise from the Au TEM grid, NaEt₃BH, and the perchlorate anion, respectively. The peak magnitudes and positions are consistent with prior EDS studies of particles in this size range.^{36,44,45} We also attempted to verify the oxidation state of the Ni DENs using electron energy loss spectroscopy (EELS) and X-ray photoelectron spectroscopy (XPS), but these experiments failed due to poor sensitivity. Specifically, the escape depth of a Ni photoelectron is 1.4

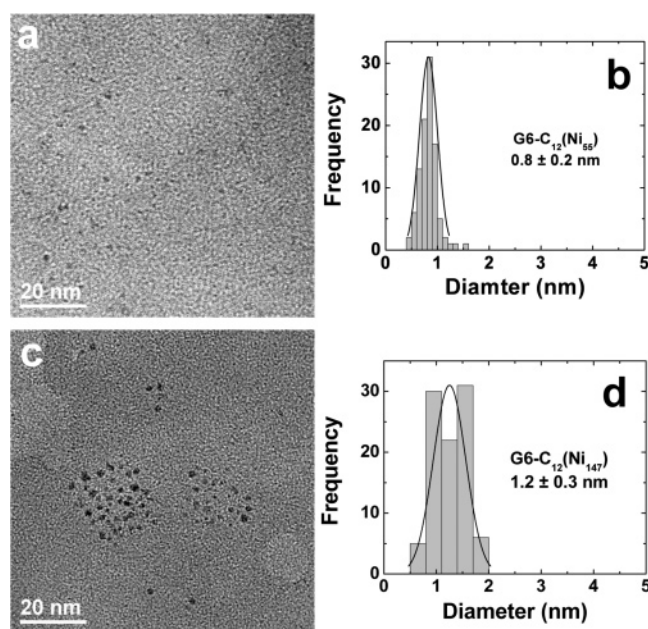


Figure 2. TEM micrographs and particle-size distributions for G6-C₁₂(Ni₅₅) (a and b, respectively) and G6-C₁₂(Ni₁₄₇) (c and d, respectively) prepared in toluene.

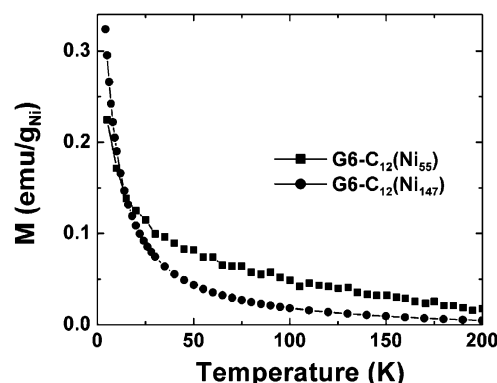


Figure 3. Field-cooled magnetization analysis of G6-C₁₂(Ni₅₅) and G6-C₁₂(Ni₁₄₇) DENs. The data were obtained using a 500 Oe magnetic field at $T < 200$ K.

nm, which is approximately one-third the radius of the dendrimers used to encapsulate the nanoparticles.⁴⁶ The sensitivity of EELS was insufficient, presumably because of the low percentage of Ni in the DENs (~ 0.62 wt % Ni for G6-C₁₂(Ni₁₄₇)).

Magnetic Analysis of Ni DENs. The magnetic properties of Ni DENs were studied using SQUID magnetometry at temperatures ranging from 5 to 300 K with a magnetic field (H) strength of 500 Oe (Figure 3). At ~ 200 K, the apparent Curie temperature, the effect of thermal energy on the magnetic properties of the DENs becomes apparent. That is, at $T > 200$ K no magnetic moment (M) is observed, indicating that the magnetic poles of the Ni particle are not aligned. However, at $T < 200$ K there is a monotonic increase in M for both sizes of Ni DENs. The low values of the Curie temperature and M can be related to the small size of the Ni particles and the energy required for magnetic pole alignment. As the energy of pole alignment approaches kT ,

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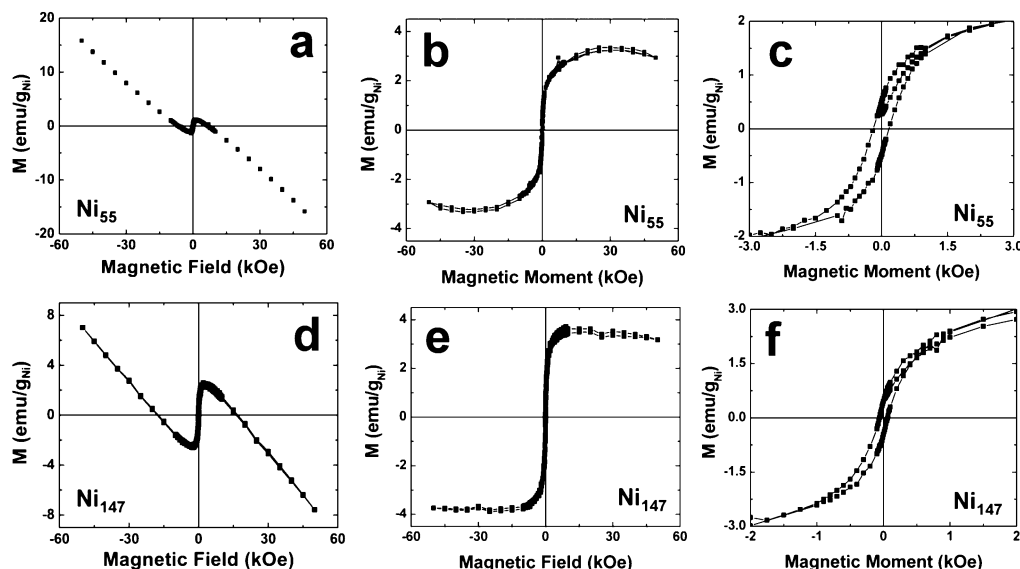


Figure 4. Magnetic moment (M) of G6-C₁₂(Ni₅₅) (a–c) and G6-C₁₂(Ni₁₄₇) (d–f) DENs as a function of the applied magnetic field. Loops (a) and (d) reveal a significant diamagnetic signal attributable to the dendrimer template at high fields, which has been subtracted from the loop in parts (b) and (e), respectively. Parts (c) and (f) show expanded views of the corresponding low-field regions. All analyses were carried out at 5 K.

thermal energy reduces the magnetic moment by disrupting alignment. Previous experimental studies have reported such temperature effects for Ni particles having diameters of 4.0 and 9.2 nm.^{18,47}

M – H loops for Ni DENs obtained at 5 K are provided in Figure 4. At fields higher than 3 kOe and lower than –3 kOe, the M – H plots have negative slopes for both G6-C₁₂–(Ni₅₅) (part a of Figure 4) and G6-C₁₂–(Ni₁₄₇) (part d of Figure 4). This feature is a consequence of the presence of the diamagnetic reaction materials that dominate the magnetic properties of the DEN composites in this range of fields. Between ± 3.0 kOe, the M – H plots reveal the ferromagnetic characteristics of the Ni nanoparticles.

To confirm these conclusions, we obtained an M – H loop for a mixture containing the dendrimer and all other components of the reaction mixture except for Ni²⁺. The results of this control experiment indicated that the precursor mixture gives rise only to a diamagnetic signal (Supporting Information, Figure S3). Accordingly, we conclude that the ferromagnetic behavior in the ± 3 kOe range (Figure 4) can only be attributed to the Ni nanoparticles.

Parts b and e of Figure 4 provide views of the background-subtracted M – H data for G6-C₁₂–(Ni₅₅) and G6-C₁₂–(Ni₁₄₇) DENs, respectively. It is evident from these results that Ni DENs are ferromagnetic with magnetic saturation values (M_s) of 3.40 emu/g_{Ni} for Ni₅₅ and 3.95 emu/g_{Ni} for Ni₁₄₇. These values are significantly smaller than the bulk value for Ni of 55 emu/g_{Ni} at 300 K.⁴⁸ The effect of the particle size is responsible for the majority of the suppression, while the passivating agent (the dendrimer) may also suppress M_s to some degree.²¹

As mentioned in the previous paragraph, the size of Ni particles affects the magnitude of their magnetic saturation. This is particularly true for particles smaller than the Ni single-domain size of 55 nm.⁴⁹ For example, Ni particles

having diameters of ~ 4 nm were found to exhibit M_s values of 27.7 emu/g_{Ni} at 5 K.¹⁸ Incomplete coordination of Ni atoms on the surfaces of these small particles, and the corresponding spin disordering, has been invoked to account for the suppression of M_s .^{18,47,48} Because the majority of the Ni atoms in the two DEN sizes studied here are on the particle surface (76% and 63% surface atoms for G6-C₁₂–(Ni₅₅) and G6-C₁₂–(Ni₁₄₇), respectively), this effect is likely to exert a major influence on their measured M_s values. Interestingly, de Heer et al. have reported that particle size is inversely proportional to saturation for nonpassivated, gas-phase Ni clusters having less than 150 atoms.³¹ However, it is difficult to compare the results reported by de Heer et al. to those reported here because of major differences in the synthesis of the materials and the conditions under which they were studied. As previously discussed, our results are more consistent with reports for materials that were synthesized and characterized under similar conditions to those we used.^{18,47}

In addition to size, ligands attached to the nanoparticle surface also affect M_s by demagnetizing the surface Ni atoms. For example, adsorption of TOPO has been reported to substantially demagnetize 4.5 nm diameter Ni nanoparticles.²¹ We know from previous catalysis studies,¹ however, that a substantial fraction of the surface atoms of DENs are unpassivated by the dendrimer and therefore can contribute to the total magnetization. Accordingly, the low value of M_s for DENs having diameters of < 2 nm can probably be mainly attributed to particle-size effects rather than ligand coordination.

It is worth comparing the magnetic properties of zerovalent Ni DENs to those of NiO materials having approximately the same size. Previous studies have shown that antiferromagnetic NiO becomes super-paramagnetic at the nanoscale level.^{50,51} This change in magnetic activity likely rises from

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two sources: incomplete magnetic compensation between Ni and O⁵² and/or small super-paramagnetic metallic Ni clusters associated with the NiO material.⁵³ These effects have been studied both theoretically and experimentally, resulting in consistent observations.^{50,54} These observations include significant hysteresis (>2 kOe) and decreasing M_s values as a function of increasing particle diameter. These attributes are opposite those of the Ni DENs described here (nearly hysteresis-free $M-H$ loops and M_s increasing with particle size), indicating that the DENs are present as zerovalent metals.

Summary and Conclusions

To summarize, we have synthesized <2 nm diameter ferromagnetic Ni nanoparticles within dendrimer templates. A significant outcome of this work is that the use of hydrophobic dendrimers and organic solvents prevents oxidation of Ni and presumably other easily oxidizable metals as well. Magnetic studies of Ni DENs indicate they

are ferromagnetic and exhibit low hysteresis and suppressed magnetic saturation, both of which are directly correlated to the small size of the particles. These results are important because they provide a means for synthesizing and studying many different types of magnetic materials on length scales that have not previously been attainable. For example, we are presently studying the effect of particle size and elemental composition on the magnetic properties of monometallic and bimetallic DENs. The results will be reported shortly.

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Supporting Information Available: Time-resolved UV-vis spectroscopic analysis of Ni DENs, EDS spectra of Ni DENs, and an $M-H$ loop for the diamagnetic reaction materials. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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