Synthesis, Characterization, and Magnetism of Dendrimer Encapsulated Co Nanoparticles

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Preparation and characterization of magnetic Co dendrimer-encapsulated nanoparticles (DENs) have been studied. As these materials are easily oxidized, the synthesis was carried out under anaerobic conditions in organic solvents. Using a hydrophobically modified G6-PAMAM dendrimer template, DENs consisting of 55 and 147 Co atoms were prepared using a single-phase direct reduction technique. Characterization of the DENs by UV-vis spectroscopy and transmission electron microscopy (TEM) indicated the synthesis of particles. The materials are nearly monodisperse with average particle diameters > 0.9 nm with dispersities of 0.2 nm. Magnetic studies of both sized DENs indicate that they are superparamagnetic with hysteresis-free magnetism. These resultant effects are directly correlated to the particle size, which has been shown to significantly affect their resultant behavior.

Introduction

Dendrimer-encapsulated nanoparticles (DENs) are synthesized by a template approach in which metal ions are loaded into the interior of polyamidoamine (PAMAM) dendrimers and then chemically reduced. This effect yields nearly size-monodisperse particles having dimensions of less than 3 nm.[2] This method was initially demonstrated by preparation of Cu clusters, but the approach was further applicable to many other transition metals including Pt, Pd, Au, and Ag.[3,7,12,13]

We have previously shown that DENs can be rendered soluble in a variety of solvents by controlling the chemistry of their periphery.[4] The chemical composition of the peripheral groups on the dendrimer described here were modified to contain dodecyl groups which provided a means for solubilizing them in organic solvents. This hydrophobic characteristic allows for production of DENs of easily oxidizable metals, such as Co. Production of such particles was previously unable to be performed under aqueous conditions. DENs composed of easily oxidizable metals are of particular interest because of their superparamagnetic properties. An advanced understanding of these DENs will pave the way for bimetallic DENs composed of alloyed mixtures of these metals as precursors and moreover, preparation of these DENs will expand the range of studies in catalysis, magnetism, and optics.

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Experimental Section

Materials. Amine terminated, sixth-generation PAMAM dendrimers substituted on the periphery with dodecyl functional groups (G6-C_{12}) were purchased from Dendritech (Midland, MI) as a 10.0% wt solution in toluene. The manufacturer indicates that 50% of the 128 H atoms on the surface of the dendrimer are substituted by dodecyl groups. Prior to use, the toluene was

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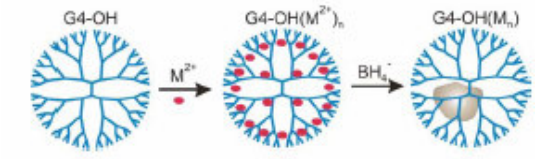
removed under vacuum at 25ºC, and a 200 µM stock solution of G6-C_{12} was prepared in toluene. $CoCl_2$, THF, and $NaEt_3BH$ were purchased from the Aldrich Chemical Company (Milwaukee, WI) and used as received.

Characterization. UV-Vis absorbance spectra were obtained using a Hewlett-Packard HP8453 spectrometer and quartz cuvettes having a pathlength of 1.00 cm. The spectrum of either toluene or THF was used as a reference depending on the solution being analyzed. Transmission electron microscopy (TEM) images were obtained using a JEOL-2010F TEM operating at 200kV and having a resolution of 0.14 nm. Samples were prepared by dropwise addition of the sample onto a holey-carbon–coated Cu grid (EM Sciences, Gibbstown, NJ).

Preparation of Co DENs. 50 µL of the 200 µM G6-C_{12} stock solution was diluted in toluene or THF to a concentration of 2.00µM. The dendrimer/metal ion complexes (G6-$C_{12}(Co^{2+})_{55}$ and (G6-$C_{12}(Co^{2+})_{147}$ were prepared by introducing 55 or 147 mol equiv., respectively, of a freshly prepared 38.0 mL $CoCl_2$ solution in THF to the dendrimer solution. The final volume of these solutions was 5.00 mL. After stirring the solutions for 5 min., 100 µL of a 1.0 M $NaEt_3BH$ solution in toluene was added to finalize the synthesis of the Co DENs. 5 minutes elapsed after reduction before the DENs were analyzed.



Results and Discussion

It has been previously shown that Au nanoparticles could be synthesized within hydrophobic dendrimers.[13] To expand their use, we exploited this functionality to produce DENs of the easily oxidizable metal Co. By this production method, in organic solvents under anaerobic condtions, oxidants such as water and oxygen can be removed from the system preventing premature particle oxidation.

Co DENs were prepared in toluene and THF by an addition of $CoCl_2$, to a 2.0 µM solution of G6-C_{12} prepared under nitrogen. This solution yielded a pale blue color and no visual evidence of precipitation. After reduction, the solution turned a deep brown color with no further evidence of precipitation. Reduction occurred rapidly after the addition of the $NaEt_3BH$.

UV-vis spectra obtained after each step of synthesis of G6-$C_{12}(Co_{55})$ are provided in Figure 1. There is an apparent difference in the bands as well as wavelength shift of each spectra which indicates the breaking and formation of bonds as the solutions differ.

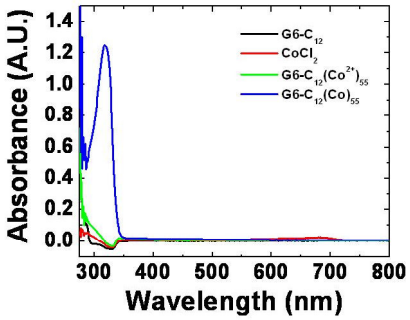


Figure 1. UV-Vis spectra of G6-$C_{12}(Co_{55})$ before and after reduction. Also shown are G6-C_{12} alone and a 110 µM spectra of $CoCl_2$.

Figure 2 shows the TEM images and particle-size distributions for G6-$C_{12}(Co_{55})$ and G6-C12(Co_{147}). Analysis of over 100 particles yielded sizes of 0.9 ± 0.2 and 1.2 ± 0.2 nm for Co_{55} and Co_{147} DENs respectively. These diameters are comparable to the calculated diameters of G6-$C_{12}(Co_{55})$ and G6-$C_{12}(Co_{147})$. which are 0.9 and 1.3 respectively.[2]

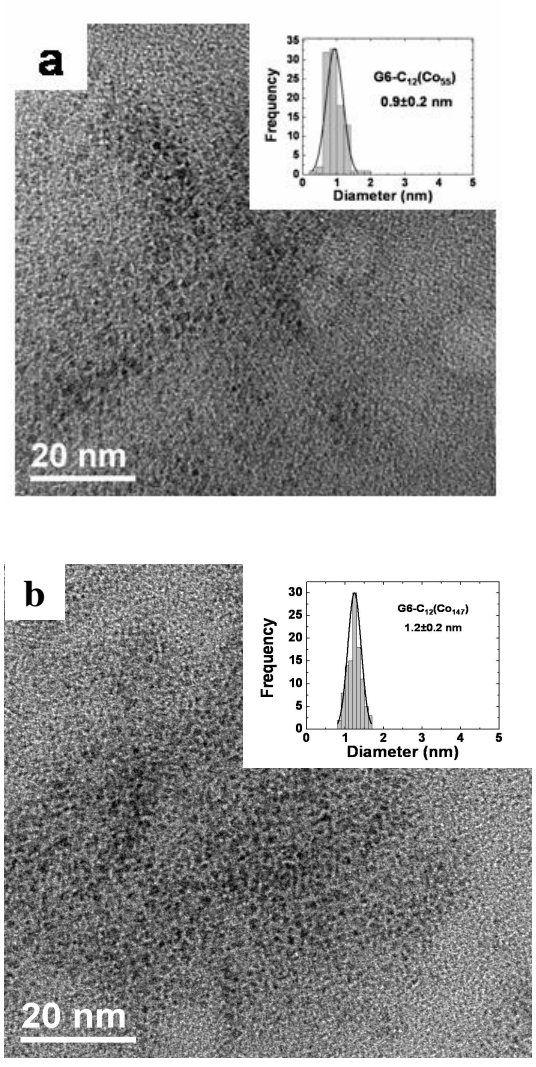


Figure 2. TEM images and size distribution for G6-$C_{12}(Co_{55})$ (a).and G6-$C_{12}(Co_{147})$ (b).

Conclusion. It is evident that dendrimer-encapsulated nanoparticles have been synthesized according to characterization. Dendrimer-encapsulated Co nanoparticles are expected to yield superparamagnetic activity with hysteresis–free magnetism in agreement with previous studies performed on Ni DENs.[15] We have shown that DENs composed of easily oxidizable metals such as Co can be synthesized within hydrophobic dendrimer templates. Characterization of these DENs paves the way for innovative applications in the fields of magnetism and catalysis. Studies concerning bimetallic Co nanoparticles are underway and will soon be reported. Together, these studies represent an advancement in understanding the effects of the nanoscale on magnetic materials. This effect is important due to the viability of magnetic storage devices as the recordable surface area decreases towards the superparamagnetic domain.

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