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Cobalt - poly(amido amine) superparamagnetic nanocomposites

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Abstract

Metallic cobalt-dendrimer nanocomposites were prepared using generation 5 Poly(amido amine) dendrimers with primary amino termini. Cobalt loading of ~38 atoms per dendrimer was determined by atomic absorption spectrophotometry. Magnetic properties of the cobalt-dendrimer nanocomposites were investigated across the temperature range from 2–300 K by SQUID magnetometry. Magnetization as a function of temperature and applied field strength was studied in zero field cooled samples. Magnetization-demagnetization curves (hysteresis loops) were also acquired at temperatures between 10 – 300 K. These results clearly indicate superparamagnetism for the nanocomposites with a characteristic blocking temperature of ~50 K.

Keywords

Cobalt; Dendrimer; Nanocomposites; Magnetic materials

1. Introduction

Several research groups have prepared dendrimer-metal nanocomposites [1–19]. The internal tertiary nitrogens of poly(amido amine) (PAMAM) dendrimers are well suited to the formation of complexes with transition metal and noble metal ions at the appropriate pH. By reduction of chelated cations, metals are trapped within the internal hydrophobic void spaces, thus forming a metal-dendrimer nanocomposite. We prepared metallic cobalt-dendrimer nanocomposites using generation 5 PAMAM dendrimers with primary amino termini (G5-NH₂). Nanocomposites were prepared by complexation of a water soluble cobalt salt, followed by reduction to the zero valent state using sodium borohydride (NaBH₄). Complex formation was confirmed by UV-visible spectrophotometry. Cobalt loading of ~ 38 atoms/dendrimer was determined by atomic absorption spectrophotometry (AAS). Magnetic properties of the cobalt-dendrimer nanocomposites were investigated across the temperature range from 2–300 K by SQUID magnetometry.

2. Experimental

Co(II)-dendrimer chelates were obtained using Co(II) chloride solutions. The complexation of Co(II) by nitrogen atoms within the dendrimer was indicated by an absorbance peak at 636 nm which was absent in separate dendrimer and Co(II) solutions. Small volume (3 mL) aqueous solutions containing 0.1272 mM G5-NH₂ and 6.8 mM CoCl₂ were prepared and pH adjusted

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to 7.0 with HCl. Co(II) was reduced to the metallic state using a 5 fold excess of NaBH₄. After 30 minutes, free cobalt metal which precipitated from solution was removed using a 0.2 μ m syringe filter. (Experiments confirmed that, in the absence of dendrimers, metallic cobalt particles prepared in similar fashion were completely removed from the filtrate.) Colloidal metallic cobalt - dendrimer nanocomposites in the filtrate were separated by ultrafiltration. Samples were dissolved in HNO₃ and Co was determined by AAS. Cobalt:dendrimer ratios were calculated based on the assumption of 100% recovery of the original dendrimer concentration on the ultrafiltration membrane. The filtrate contained 38.2 cobalt atoms per dendrimer, corresponding to 71.5 % of the cobalt atoms originally in solution. Materials prepared in this manner were stored under an N₂ atmosphere to prevent oxidation of the Co-PAMAM dendrimer nanocomposite. Magnetic properties of the resulting nanocomposites were studied by SQUID magnetometry. Measurements were acquired on three gelatin encapsulated samples, including: 1) a method blank consisting of a gelatin capsule containing 26.6 mg of G5-NH₂ dendrimer; 2) a precipitated metallic cobalt sample containing 0.57 mg of metallic cobalt; and 3) a cobalt-G5-NH₂ dendrimer nanocomposite containing 57.21 mg of sample (7.24 % cobalt).

3. Results and Discussion

To establish superparamagnetism of the nanomaterials, it was necessary to characterize the relationship between magnetic susceptibility and temperature to identify a characteristic blocking temperature (T_b). Below the blocking temperature, the material exhibits ferromagnetic phenomena, including hysteresis and remnant magnetization. The cobalt - G5-NH₂ dendrimer nanocomposite sample was first cooled at zero magnetic field to 2 K, followed by application of a constant magnetic field and collection of a series of magnetic measurements as the temperature was increased. Zero field cooled (ZFC) magnetization curves at 10, 50, and 250 Oe are shown in Fig. 1 for temperatures between 2 and 300 K. All three curves indicate a T_b value of $\sim$ 50 K. Below T_b , the cobalt-G5-NH₂ dendrimer nanocomposite displays ferromagnetic behavior which is evident from the hysteresis loop recorded at 10 K and shown in Fig. 2. Figs. 3 and 4 present additional magnetization-demagnetization curves acquired below T_b at 40K, and above T_b at 300 K, respectively. As the temperature is raised toward T_b , the degree of hysteresis progressively diminishes, with decreasing values for both the coercive field, H_c , and remnant magnetization, M_r . For example: at 10 K, H_c equals 735 Oe and M_r is 65 emu/g. As the temperature rises to 20 K, H_c falls to 288.3 Oe and M_r is lowered to 43 emu/g. At 30 K, H_c further decreases to 94.5 Oe and M_r falls to 24.6 emu/g. Just slightly below T_b at 40 K, H_c falls to 33.8 Oe and M_r equals only 10.4 emu/g. Above T_b , no hysteresis or remnant magnetization is observed. In all cases, the saturation magnetization values are similar, ranging from 153 to 159 emu/g.

M_s at 10 K is 159.6 emu/g, corresponding to a magnetic moment per atom of 1.68 μ_B , as compared to 1.72 μ_B for bulk cobalt, where μ_B is the Bohr magneton. This magnetic moment is somewhat low, most probably due to a slight over estimation of the zero valent cobalt mass, stemming from a minor degree of oxidation of the sample. The blocking temperature of $\sim$ 50 K is clearly indicated by the three ZFC curves obtained over a range of field strengths (Fig. 1), and by the magnetization-demagnetization curves acquired above (Fig. 4) and below T_b (Figs. 2 and 3). The ZFC data indicate no change in T_b with changes in applied field. As expected, the magnetization increases with the intensity of the applied magnetic field. Superparamagnetic behavior of the Co-PAMAM nanocomposite is further confirmed by a plot of inverse magnetization versus temperature (Fig. 5) which clearly indicates that Curie Law paramagnetic behavior is observed at temperatures above 50 K.

An estimate of the magnetic particle size was made from these data using the Langevin equation which expresses magnetization as a function of H/T ,

$$M = M_s \left[\frac{1 + \exp\left(-2 \frac{M_s V \rho \mu_o H}{k_B T}\right)}{1 - \exp\left(-2 \frac{M_s V \rho \mu_o H}{k_B T}\right)} \right] \quad (1)$$

where V is particle volume, ρ is cobalt density, μ_o is the permeability of free space, H is the magnetic field strength, and T is absolute temperature. Using the measured values for magnetization and saturation magnetization, Equation (1) was solved for particle volume, indicating a particle diameter of ~ 4 nm. This corresponds roughly to the diameter of the G5-PAMAM dendrimer.

3. Conclusions

Generation 5 amino terminated cobalt – poly(amido amine) dendrimer nanocomposites were successfully prepared. Magnetization as a function of temperature and applied field strength was studied in Zero Field Cooled samples, indicating superparamagnetism above the characteristic blocking temperature of 50 K. This was confirmed by a series of magnetization-demagnetization curves acquired at temperatures between 10 – 300K, indicating both remnant magnetization and hysteresis phenomena below the blocking temperature and the absence of these above the blocking temperature. Further, above 50 K the cobalt-dendrimer nanocomposites were shown to obey the Curie Law for paramagnetic materials. Using the Langevin equation, a particle size of ~ 4 nm was estimated for Co-G5-NH₂. At ambient temperature, the resulting superparamagnetic cobalt-dendrimer nanocomposites exhibit strong magnetic susceptibility with no remnant magnetization. Thus the magnetic nanocomposites are extremely small particles which are easily magnetized and demagnetized. Since they bear numerous branches upon which antibodies and enzymes can be attached, they are excellent candidates for further investigations regarding enzymatic and immunochemical recognition, isolation, quantitation, and other biomedical and therapeutic applications.

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Fig. 1. Magnetization versus temperature relationships for Zero Field Cooled (ZFC) samples of Co-G5-NH₂ at field strengths between 10–250 Oe

Fig. 2.
Magnetization-demagnetization curves at 10 K for Co-G5-NH₂ nanocomposite

Fig. 3.
Magnetization-demagnetization curve at 40 K for Co-G5-NH₂ nanocomposite

Fig. 4. Magnetization-demagnetization curve at 300 K for Co-G5-NH₂ nanocomposite ($M_r = 0$)

Fig. 5. Inverse magnetization versus temperature relationship for Co-G5-NH₂ nanocomposite demonstrates Curie Law paramagnetic behavior above T_b .