Fabrication of Novel Magnetic Nanoparticles for Rare-earth-Free Permanent Magnets

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Introduction
Magnetic nanoparticles (NPs) and their broad range of applications is one of the most useful aspects of nanotechnology. They are a class of nanoparticles which typically less than 100 nm in all dimensions. Such particles commonly consist of magnetic elements such as iron, nickel and cobalt and their chemical compounds. The Magnetic nanoparticles have been the focus of much research recently because they possess attractive properties which could see potential use in catalysis, biomedicine, magnetic resonance imaging, magnetic particle imaging, data storage and environmental remediation.

Rare earth metals, although are not very rare, and their magnetic alloys which were developed in the 1970s and 1980s are substantially stronger than ferrite (chemical compounds, ceramic with iron(III) oxide as their principal components) or Alnico (iron alloys with aluminum (Al), nickel (Ni) and cobalt (Co) primarily) magnets. The magnetic field typically produced by rare-earth magnets can be in excess of 1.4 teslas, whereas ferrite or ceramic magnets typically exhibit fields of 0.5 to 1 tesla. Their common applications include: computer hard drives, audio speakers and permanent magnet motors in cordless tools. There are two main types of rare-earth magnets: neodymium-iron-boron magnets and samarium-cobalt magnets. The samarium-cobalt magnet is one of the strongest magnets made, but Samarium is very expensive. Soft (low resistance against aligning in direction of an applied magnetic field) magnets like FeCo possess very high magnetic moments. Our overall goal is to synthesize magnetic nanocomposite of FeCo and SmCo with a lower manufacturing cost and high “energy product” $(BH)_{\text{max}}$ (maximum magnetic energy stored in a magnet). To attain that goal FeCo have been fabricated in a non-aqueous solution (ethylene glycol as the solvent) with a high moment.

Experimental Details
FeCo NPs were synthesized using the polyol method. Stoichiometric quantities of iron chloride; cobalt acetate and sodium hydroxide were mixed and added to 100 mL of ethylene glycol which served as solvent and surfactant simultaneously. The mixture was stirred and heated to reflux (the beaker was covered with aluminum foil) to 200 °C to form NPs. Then the mixture was cooled to room temperature by removing the heat source. Particles then were separated from the mixture by means of magnetic separation and ultrasonification for 1.5 hours. After removing the supernatant, the precipitate was rinsed with methanol and centrifuged at 5000 rpm for 5 min several times. Finally, the precipitate was dried in an oven overnight at 50 °C. The particles were characterized by Vibrating Sample Magnetometry (VSM), X-Ray Diffraction and High Resolution Transmission Electron Microscopy (HRTEM) to examine the magnetic properties, composition and surface morphology of the samples, respectively. HRTEM was carried out by our collaborators at University of Delaware and Virginia Commonwealth University.

Results and Discussion
FeCo particles are obtained from reduction of their salts at high temperatures (usually at the boiling temperature of the solvent; in this case 200 °C). We examined two possible synthesis conditions; adding the reactant to the cold solution and then heating the solution or, injecting the reactants into a pre-heated solution at 200 °C. The VSM and XRD results show that in latter condition particles have higher moments than the former one (219 emu/g vs. 149 emu/g). Additionally, in the first condition, some secondary phases were detected by X-ray diffraction. After choosing the pre-heating mixing condition as our operating condition, we investigated the effect of two important parameters; the reaction time and the salt-metal precursor concentration ratio. First, an increase in reaction time from 1 min to 60 min (1, 7, 15, 25, 30, 40, 50, and 60 min) it was found that magnetic moment increases until about 30 min and then starts to decrease. It is speculated that the reason for this behavior is particle
oxidation. XRD patterns confirmed this hypothesis as it is noted that cobalt oxide and iron oxide form when the reaction time exceeds 40 min. Simultaneously, FeCo Bragg diffraction peaks begin to weaken and disappear at longer reaction times.

The other synthesis processing parameter that was varied was the salt concentration. According to the literature, hydroxyl ions provide active sites for nucleation and growth of the FeCo nanoparticles. At low salt/metal concentration ratio (12:1), the obtained nanoparticle moment was much lower than expected. It is believed that it is due to the low amount of nuclei formed and the formation of immature particles less than 10 nm in diameter which have a low moment. With an increasing salt-metal ratio, the nanoparticles moment increases. At the ratio 27:1 the nanoparticles moment reaches its highest value at 219 emu/g. This value may be compared with that of bulk FeCo which is 240 emu/g. At this ratio, we obtained uniform particles with 15-25 nm diameters. On the other hand, as salt-metal precursor ratio exceeded 40, the nanoparticles magnetic moment begins to decrease. It is believed that this effect is due to the high amount of hydroxyl and oxygen ions that facilitates other reactions such as oxidation. In this case XRD analysis shows the formation of secondary phases such as iron oxides.

Figure 1. Effect of reaction time on magnetic moment

Figure 2. Effect of salt to metal ratio on magnetic moment

In conclusion, the highest magnetic moment of the FeCo nanoparticles was obtained with the salt-metal ratio at 27:1 and after 30 minutes reaction. As the reaction time increases to above 40 min, formation of iron and cobalt oxides decreases the nanoparticles magnetic moment. Future works include increasing the nanoparticle magnetic moment to more than 230 emu/g and obtaining particles with 20-30 nm diameters.

References