Synthesis and Characterization of Cobalt Nanoparticles

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Abstract

Numerous physical and chemical methods have been developed for the preparation of magnetic nanoparticles. Here we have discussed synthesis of cobalt nanoparticles by using inverse micelle technique at room temperature. Cobalt nanoparticles were prepared by the reverse micelle technique (NaBH₄ reduction of cobalt chloride in a reversed micelle solution of didodecylammoniumbromide (DDAB)/Toluene and CTAB/Toluene). The size of cobalt nanoparticles could be easily controlled by changing the water contents and micelle concentrations. Super paramagnetic cobalt nanoparticles (4.3nm) have been obtained by this method where coercivity is 8.34 gauss.

Introduction

Many properties of solids depends on the size range over which they are measured. When measurements are made in the micrometer or nanometer range, many properties of material change. Owing to nanometer scale size these particles lead to change in physical and chemical properties which could be utilized in many important applications. Magnetic particles of micro and nanometer size are attracting growing fundamental and technological interest. Magnets are important for motors, electrical power transformation, data storage devices, electronics etc. One of the important features of modern technology requires extremely small magnet of micro or even nanometer size. How to prepare such materials? Which properties can one expect from an extremely small piece of a material which is ferromagnetic in bulk state? These are the important issues to be understood.

In nature there are only three ferromagnetic elements at room temperature, viz. Iron, cobalt and nickel (one can also include in this series gadolinium which is ferromagnetic below 16 °C). Additionally, some compounds and alloys of manganese and chromium can exhibit ferri and ferromagnetic behavior. Magnetic nanoparticles could find future applications also as catalysts and single electron devices. Also possibility of manipulating nanoparticles at a distance by applying an external magnetic field opens up a broad field for biomedical application of magnetic nanoparticles.

Specific surface groups of the stabilizers can be used for linking different species to the nanoparticle surface. Drugs and antibodies can be attached to the surface of colloidal magnetic nanoparticles and can be steered into regions of the body where they are required by means of an external applied magnetic field. Functionalized magnetic nanoparticles can be specifically attached to a cancer tumor and heated up by a magnetic field, resulting in thermoablation of the tumor.

The preparation of nanoparticles of desired sizes is the first and very important step. Narrow size distribution or monodispersity is highly desirable because magnetic properties become strongly size dependent in the nanometer size range. Numerous physical and chemical methods have been developed for the preparation of magnetic nanoparticles. Bloomfield et. al. [10] and De Heer et. al. [11] employed laser ablation methods and prepared magnetic nanoparticles (Co, Ni, Fe) of 40-500 atoms. The different preparation methods lead to magnetic nanoparticles with differences in crystalline structure, and its shape. The fabrication technique has a great influence on the magnetic properties of the materials obtained.

One of the methods which is commonly used for preparation of magnetic nanoparticles is water_in_oil microemulsion (reverse micelles) technique which is based on using droplets of water sustained in an organic phase by a surfactant. A metal salt dissolved in the nanodroplets can be reduced inside these nanometer sized reactors to metal nanoparticles [1, 2].

Petit and pileni prepared cobalt nanoparticles by mixing two miceller solutions after subsequent standard treatment they obtained cobalt nanoparticles of 5.8 nm [9].

Lec and Choi have done the same synthesis at room temperature and obtained cobalt nanorods [2]. In another paper Krishnan has studied magnetic nanoparticles and coreshell stractures and dilute magnetic dielectrics, a new class of materials for spin electronics application [12].

Experimental

Cobalt nanoparticles were prepared by the reverse micelle solution technique (NaBH₄ reduction of cobalt chloride in a reversed micelle solution of (DDAB or CTAB / toluene))
All the synthesis steps were carried out in N₂ environment during the reaction to avoid passable oxygen contamination. Dried toluene and deionized water were bubbled with N₂ gas for two hours before experiment then. In 25mL two neck flask, DDAB or CTAB then (1.5 g, 3 mmol) was dissolved in 10 mL of dried-toluene to form 0.3 M reverse micelle solution. This reverse micelle solution was solicited to make a clear solution and CoCl₂ (25 mg, 0.1 mmol) is added. The mixed solution was then solicited until the entire solid disappeared and blue solution was obtained NaBH₄ (113 gm) was dissolved in 3 ml of deionizer water to prepare 1M solution and 300 µL of 1 M NaBH₄ solution was slowly added to reverse micelle by using micro syringe. A black colloid solution appeared after 1 min.

Reaction:

\[2\text{CoCl}_2+10\text{NaBH}_4+9\text{H}_2\text{O} \rightarrow \text{Co}_2\text{B}+12.5\text{H}_2+3\text{B(OH)}_3+4\text{NaCl}\]

\[4\text{Co}_2\text{B}+3\text{O}_2 \rightarrow 8\text{Co}+2\text{B}_2\text{O}_3\]

Cobalt nanoparticles were synthesized with different surfactants and also different concentration of surfactants and their size and magnetic properties were studied by XRD and VSM. X-ray diffraction is performed on Philips pw 1840 powder diffractometer. The system is equipped with an X-ray tube, nickel filter, sample holder and the detector here we have used CuKα (1.54) radiation.

In the VSM system which we have done our analysis field varies to 2 tesla and frequency of vibrating sample is 85Hz and the set up is room temperature set up. (Temperature can varry from 10K to 1000°C.)

Particle size is calculated by using scherer formula from XRD.

Scherer formula: [7]

\[d = \frac{0.9\lambda}{B\cos\theta}\]

Where:
\(d\) : particle size  
\(\lambda\) : wavelength of CuKα  
\(\theta\) : peak angle  
\(B\) : FWHM of cobalt peak

Result:

Value of magnetization and coercivity of each sample has given in table (1).
By XRD data we get two peaks one for cobalt at 45.4 and one for cobalt oxide at 31.8 °. The size of the cobalt nanoparticle is 4.3 nm.

By XRD we get two peaks, one for cobalt at 45.6 and one is cobalt oxide at 32.° and size of cobalt nanoparticle is 4.9nm.
Table (1)

<table>
<thead>
<tr>
<th>Particle size (nm)</th>
<th>Magnetization (emu/gram)</th>
<th>Magnetization (emu/atom)</th>
<th>Remanent magnetization (emu/gram)</th>
<th>Coercivity (gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45.3</td>
<td>3.03</td>
<td>0.030µB</td>
<td>0.275</td>
<td>71.548</td>
</tr>
<tr>
<td>44.9</td>
<td>7.45</td>
<td>0.079µB</td>
<td>0.520</td>
<td>69.82</td>
</tr>
<tr>
<td>44.7</td>
<td>3.54</td>
<td>0.037µB</td>
<td>0.236</td>
<td>68.84</td>
</tr>
<tr>
<td>42.3</td>
<td>2.81</td>
<td>0.029µB</td>
<td>0.369</td>
<td>68.56</td>
</tr>
<tr>
<td>35.2</td>
<td>1.78</td>
<td>0.018µB</td>
<td>0.169</td>
<td>66.69</td>
</tr>
<tr>
<td>21.6</td>
<td>2.07</td>
<td>0.021µB</td>
<td>0.111</td>
<td>58.39</td>
</tr>
<tr>
<td>21.1</td>
<td>1.09</td>
<td>0.011µB</td>
<td>0.134</td>
<td>63.19</td>
</tr>
<tr>
<td>4.9</td>
<td>3.20</td>
<td>0.033µB</td>
<td>0.321</td>
<td>34.52</td>
</tr>
<tr>
<td>4.3</td>
<td>2.86</td>
<td>0.029µB</td>
<td>26.227E-3</td>
<td>8.34</td>
</tr>
</tbody>
</table>

Graph (1): coercivity versus particle size

From graph (1) by increasing the particle size coercivity increases and in case of cobalt nanoparticles with 4.3 nanometer coercivity is 8.347 which is very less and we get superparamagnetic behaviour for cobalt nanoparticles .fig(e)

Table (2): Different surfactants

<table>
<thead>
<tr>
<th>surfactant</th>
<th>PARTICLE SIZE(NM)</th>
<th>COERCIVITY (GAUSS)</th>
<th>MAGNATIZATION (EMU/ATOM)</th>
<th>REMANENT MAGNETIZATION (EMU/GRAM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB</td>
<td>21.1</td>
<td>63.19</td>
<td>0.011µB</td>
<td>0.134</td>
</tr>
<tr>
<td>DDAB</td>
<td>21.6</td>
<td>58.39</td>
<td>0.021µB</td>
<td>0.111</td>
</tr>
</tbody>
</table>

From table by using DDAB magnetization of particles per atom is more and coercivity is less in compare with using CTAB as a surfactant.

Table (3): CTAB surfactant with different concentrations

<table>
<thead>
<tr>
<th>surfactant</th>
<th>PARTICLE SIZE(NM)</th>
<th>COERCIVITY (GAUSS)</th>
<th>MAGNATIZATION (EMU/ATOM)</th>
<th>REMANENT MAGNETIZATION (EMU/GRAM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB</td>
<td>4.9</td>
<td>34.52</td>
<td>0.033µB</td>
<td>0.321</td>
</tr>
<tr>
<td>CTAB (2 TIMES)</td>
<td>4.3</td>
<td>8.34</td>
<td>0.029µB</td>
<td>26.227E-3</td>
</tr>
</tbody>
</table>
From table by using 2 times CTAB particle size, magnetization, coercivity and remanent magnetization decrease.

<table>
<thead>
<tr>
<th>surfactant</th>
<th>PARTICLE SIZE (NM)</th>
<th>COERCIVITY (GAUSS)</th>
<th>MAGNETIZATION (EMU/ATOM)</th>
<th>REMANENT MAGNETIZATION (EMU/GRAM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDAB</td>
<td>21.6</td>
<td>58.39</td>
<td>0.021µB</td>
<td>0.111</td>
</tr>
<tr>
<td>DDAB (2 TIMES)</td>
<td>18.6</td>
<td>42.66</td>
<td>0.010µB</td>
<td>14.88E-3</td>
</tr>
</tbody>
</table>

By using 2 times DDAB particle size, coercivity, magnetization and remanent magnetization decrease.

From results it is obvious that by increasing the particle size coercivity increases and in case of 4.3 nm size coercivity is very small and it shows superparamagnetic behavior also by using different surfactants magnetization and coercivity for almost same size particles are different and for same surfactant with different concentrations also we will have different magnetization and coercivity. Hence surfactant and concentration of surfactant also different sizes play important roles in magnetic properties. Important factor which affects particle size is temperature, by decreasing the temperature particle size also decreases.

**Discussion:**

Cobalt nanoparticles have been synthesized successfully in DDAB/water/toluene and CTAB/water/toluene inverse micelle solution. Reactions have performed at 47 to 50 °C. By controlling the temperature and changing the concentration of surfactant one can control the particle size.

By increasing the surfactant and reducing the temperature particle size decreases.

Cobalt nanoparticles can be synthesized in three different crystalline modifications:
1) hexagonal closed pack (hcp)
2) face centered cubic (fcc)
3) epsilon

The epsilon cobalt structure which is not observed in the bulk consists of a twenty atom unit cell with cubic symmetry. The hcp structure is the most stable phase for bulk cobalt at room temperature.

By observing results we conclude that:
1) By comparing ASTM data structure of cobalt nanoparticles is hcp.
2) As predicted below 5 nm cobalt shows superparamagnetic behaviour and in case of 4.3 nm size VSM data shows superparamagnetic behaviour for cobalt nanoparticles.
3) As shown in table (1) by reducing the particle size coercivity decreases.
4) The reason is that the number of spins coupled by exchange interaction decrease with the size of the single domain particle, leading to an easier spontaneous orientation of magnetization at a given temperature and thus to a decrease in coercivity.
5) Reducing the size of the single domain particle decreases the number of spin exchange coupled to resist spontaneous reorientation magnetization at a given temperature.
6) From tables (3) and (4) we have decrease in saturation magnetization by reducing particle size. The reason of the drop in saturation magnetization with decreasing in nanoparticle size was attributed to increase in nanoparticle surface to volume ratio. Saturation magnetization in case of bulk cobalt is 1.6 bohr magnetron per atom and in case of nanoparticles its vary between 0.01 and 0.03 bohr magnetron per atom for different particle sizes.
7) From XRD result we are getting two peaks where one is due to presence of cobalt and another is due to presence of cobalt oxide.
8) A serious drawback of cobalt and other elemental magnetic nanoparticles is their low stability toward oxidation under ambient conditions. Thus the exposure of cobalt nanoparticles to air results in the formation of a shell of 1-2 monolayer of cobalt oxide. The shell of antiferromagnetic cobalt oxide disturbs the magnetic properties of the cobalt core, additionally intrinsic coercivity of elemental cobalt is very low.

**References**


[5] "nanotechnology a gentle introduction to the next big idea", by Mark ratner andDaniel ratner, Prin- tic Hall, publication, 2001


[8] Dennis speliotis, ADE technologies, Inc. Newton, MA, USA


