Fabrication of Core-Shell Nanoparticles

Zhanhu Guo

Louisiana State University and Agricultural and Mechanical College, nanomaterials2000@gmail.com

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FABRICATION OF CORE-SHELL NANOPARTICLES

A Dissertation
Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy
In

The Gordon A. and Mary Cain Department of Chemical Engineering

By
Zhanhu Guo
B.S., Shandong Institute of Mining and Technology, 1996
M.S., Beijing University of Chemical Technology, 1999
December, 2005
To my peaceful family in China, my wife and my lovely son
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ABSTRACT

Metallic Cu and Au shells were fabricated around cobalt nanoparticles. A new technique to coat nanoparticles with carbon coatings and poly(methyl methacrylate) (PMMA) was developed.

The copper shell formation is a self-limiting process. A thin copper shell (0.82 nm) around the cobalt nanoparticle (1.56 nm) enhanced the magnetic property by increasing the blocking temperature from 124 K to 235 K for nanoparticles with a copper shell. The formed gold shell (0.67 nm) enhanced the cobalt nanoparticle magnetic property by increasing the blocking temperature above room temperature. The magnetic moment in the Co-Cu and Co-Au core-shell nanoparticle is much higher than that of the pure cobalt nanoparticle. However, the copper shell (2.88 nm) around the FeCo alloy nanoparticle (0.87 nm) was fabricated and found to decrease the blocking temperature to 126 K. Complete displacement of Fe nanoparticle by copper ions was observed with a loss of the magnetic property. The electrochemical reaction rate was used to estimate the reaction rate in aqueous solutions between the cobalt, or iron nanoparticle, and the copper ions and was found to be similar: 0.0015 A/cm$^2$ and 0.0022 A/cm$^2$ for the Co-Cu and Fe-Cu systems.

The annealing process has a dramatic effect on the behavior of the nanoparticles. The sizes were increased in all the nanoparticles, as expected. A phase change (from fcc to hcp) was found in the cobalt nanoparticles as the annealing temperature increased. Phase segregation and partial oxidation of the FeCo alloy nanoparticle under the annealing process was observed. A tight carbon shell was formed around the iron nanoparticle and protected the iron nanoparticle from oxidation.
in acid. Fe-C core-shell nanoparticles retained the magnetic property (i.e. saturation magnetization and coercivity) after exposure to acid.

A resistance change with a variation of magnetic field is referred to as magnetoresistance (MR). Magnetoresistance was observed in the pressed Co-Au core-shell pellet. Both the fresh Co-Au and annealed core-shell nanoparticle followed the metallic conduction behavior. No MR was observed in the Co-Cu and FeCo-Cu core-shell nanoparticles.
CHAPTER 1 INTRODUCTION

Nanoparticle fabrication has been achieved with a variety of metal systems. Noble metal nanoparticles such as gold, silver and platinum have been fabricated and applied in biological,\textsuperscript{1-4} optical,\textsuperscript{5,6} and catalytic areas.\textsuperscript{7} Pure iron-group element nanoparticles (cobalt, iron, and nickel) are of interest due to their unusual magnetic properties such as an enhanced coercivity\textsuperscript{8-10} and have potential applications such as in bio-medical\textsuperscript{11} and ultrahigh density magnetic recording media.\textsuperscript{9,12-21} Alloyed iron-group nanoparticles such as FePt,\textsuperscript{22,23} CoPt,\textsuperscript{24-26} FeCo,\textsuperscript{27} CoNi,\textsuperscript{28} CoTi,\textsuperscript{29} and CoRh\textsuperscript{30} have gained attention in high density data storage due to their inherent high magnetic anisotropy. In addition, core-shell nanoparticles were reported: Ni-Pd,\textsuperscript{31} Au-Pd,\textsuperscript{32} Pt-Au,\textsuperscript{33} Fe-SiO\textsubscript{2},\textsuperscript{34} Co-SiO\textsubscript{2},\textsuperscript{35} Pd-Pt,\textsuperscript{36} and Cu-Fe.\textsuperscript{37}

A schematic of the alloy and the core-shell structure is shown in Figure 1.1 (a) and (b), respectively. The core-shell nanoparticles can be either elements or alloys. The alloyed nanoparticles are formed if the elements form a solid solution within one single nanoparticle; otherwise, a core-shell nanoparticle structure may form. Ideally, the two metals or materials should be immiscible for the core-shell structure. The advantage of the core-shell structure is that the shell metal properties can be combined with the core metal properties. In addition, the shell can be used to protect the core material in harsh environments. For example, the shell coating prevents the nanoparticle from oxidation in air by oxygen, and in low pH solutions by protons. Attempts to protect the magnetic nanoparticle from oxidation by the use of noble metals,\textsuperscript{31,38-45} carbon\textsuperscript{46} and silica\textsuperscript{35} shells have been reported.
Magnetic nanoparticles (e.g. Co and Fe) are reactive with oxygen in air and aqueous solutions resulting in a deleterious change in magnetic properties. It was reported that the blocking temperature (the temperature, at which the superparamagnetic state transits to a ferromagnetic state) for CoO nanoparticles with a size of 4.5 nm is around 10 K, which is lower than the blocking temperature of Co nanoparticles (20 K) having a comparable size (3.3 nm). The introduction of the oxides on the metallic nanoparticle surface decreases the saturation magnetization (the magnetization when it reaches stable at high field). The saturation magnetization also decreases with the increase of the oxide content as observed in iron oxide coated iron nanoparticles. Thus, a more noble metal or other inert materials that comprise the shell will protect the more reactive core iron-group metallic nanoparticle.

The reported methods for the synthesis of nanoparticles include reverse micelle, wet chemical synthesis (reduction of halide ions by reducing agents in the presence of a surfactant), thermal decomposition of organic-metallic precursor, sol-gel, sonochemical, photochemical, cathode sputtering, and vapor deposition. Compared with other methods, the wet chemical method has the following advantages: easy operation, low cost, easy scale-up, and safer at room temperature.
The reported methods to fabricate the noble metal shell include a microemulsion technique\textsuperscript{38,43-45,63} where the metallic shell ions are reduced with a reducing agent added to the solution containing nanoparticles; the displacement reaction technique where part of the metallic core nanoparticle is sacrificed as the reducing agent for the noble metal deposition;\textsuperscript{1,40,42} and the thermal segregation technique\textsuperscript{47} where phase segregation of a metastable alloy occurs upon heat treatment. Also, a high temperature transmetallation reaction (200 °C) has been used to form a gold shell around iron nanoparticles.\textsuperscript{54} In these studies, the core-shell fabrication methods take place in organic solutions, as these are typically the solvents that are used to generate the metallic core nanoparticle in the first place. Stability of the core-shell nanoparticles is still contested, as recently pointed out by Ravel \textit{et al.}\textsuperscript{38} X-ray absorption studies (XAS) detected evidence of oxidation due to discontinuous gold coatings around iron nanoparticles fabricated using the reverse micelle synthesis approach. They speculate that this is an unintended consequence of the reverse micelle methodology.

The applications of the core-shell metallic nanoparticles include its use as a catalyst, such as the recently reported Ni-Pd core-shell nanoparticles\textsuperscript{31} possessing enhanced catalytic activity in various Sonogashira coupling reactions (for the formation of C-C bonds of terminal acetylenes molecules with halides). In addition, core-shell nanoparticles may have potential applications in fabricating granular materials for giant magnetoresistive (GMR) behavior. To date, GMR phenomena has been used in a variety of applications, including biological detection,\textsuperscript{64} magnetic recording and storage systems\textsuperscript{65} and automotive applications\textsuperscript{66} since it was discovered in 1988.\textsuperscript{67}
GMR in both the granular and the multilayered systems follow a spin-dependent scattering of the conductive electrons in the magnetic clusters. A large resistance in the material occurs when the magnetic regions are antiferromagnetically coupled with adjacent magnetic regions. Such coupling occurs when the regions are nanometric and their separation is on the nanometer scale. A decrease in the material’s resistance occurs when an applied magnetic field aligns the magnetic regions. For example, a thin film multilayer GMR material consists of alternating layers of magnetic (ferromagnetic) and non-magnetic materials (paramagnetic), as shown in Figure 1.2, in the antiferromagnetically coupled state (a) and when an external magnetic field is applied (b).

![Figure 1.2 Schematics of multilayer GMR structure (a) antiferromagnetic domain orientation and (b) parallel magnetic domains when there is an applied magnetic field.](image)

Similar to multilayered materials, a granular structure with a nanometric ferromagnetic layer separated by a non-magnetic layer is shown in Figure 1.3. There is a homogenous mixture of nanometric, ferromagnetic phases in a non-magnetic matrix. Methods to fabricate the granular alloyed films include sputtering, e-beam coevaporation, electrodeposition, and melt spinning technique. The GMR phenomena was reported to disappear if the nonmagnetic layer was thicker than the electron mean-free path, which was consistent with the prediction of the RKKY theory (an abbreviation derived from the names: Ruderman, Kittel, Kasuya and Yosida).
Polymeric nanocomposites embedded with nanoparticles have attracted much interest due to their high homogeneity, high processability and tunable optical properties. Poly (methyl methacrylate) (PMMA) is attractive due to its lighter weight, softness, flexibility, higher ultraviolet light transmission in comparison with glass, and good compatibility with human tissue normally used to replace intraocular lenses in the eye or to affix implants and to remodel lost bone. In addition, PMMA has a high glass-transition temperature at 120 °C, which allows for the formation of robust films at room temperature. The methods to incorporate magnetic nanoparticles into a PMMA matrix include ex-situ methods, i.e. by dispersing the synthesized magnetic nanoparticles into organic PMMA solution, or polymerization of methyl methacrylate monomer in the presence of the magnetic nanoparticles.

Carbon coated nanoparticles have been fabricated by the standard and modified carbon arc method, magnetron and ion-beam co-sputtering, catalytic chemical vapor deposition (CCVD), co-carbonization of aromatic heavy oil and ferrocene, thermal segregation of FeC$_2$ and of the mixture of hematite and C. The disadvantage of the standard or modified arc, co-sputtering and co-carbonization methods is the low-yield, and the presence of other carbon by-products such as carbon nanotube (CNT) or uncoated metal nanoparticles. Higher yields can be achieved with the CCVD
method, although there is the formation of unnecessary carbon nanotube or uncoated metal nanoparticles.\textsuperscript{96} The thermal segregation of FeC\textsubscript{2} method has the potential ability to obtain pure carbon coated iron nanoparticles,\textsuperscript{100} while the thermal segregation of a mixture of hematite and C produces carbon nanotubes.\textsuperscript{101} The effectiveness of the carbon shell in the protection of a nickel core nanoparticle from oxidation was evidenced by distinguishing the core-shell contrast with high-resolution TEM after an acidic (HCl and HNO\textsubscript{3}) treatment.\textsuperscript{91} It was further observed that the saturation magnetization of carbon coated iron nanoparticles decreased compared with the bulk materials\textsuperscript{92,98} and that the coercivity was lower than that for the bare iron nanoparticles\textsuperscript{100,101} but higher than that for the corresponding microcrystals.\textsuperscript{98} Thus, the introduction of a carbon shell alters the magnetic property of the iron nanoparticles.

This dissertation will focus on the (1) fabrication of Cu and Au shells around a Co core, (2) examination of the GMR effect, (3) establishing the limits and generality of the methodologies by replacing the Co core with Fe and (4) synthesizing carbon shells around iron nanoparticles. The Cu shell was fabricated in a non-traditional route, using a displacement technique in aqueous media. As compared with the conventional methods conducted in organic solution, the adopted method in the Co-Cu core-shell fabrication is cheaper, the shell was “tighter”, and the particle was more stable. Gold shells fabricated from a displacement reaction were also used to protect the cobalt nanoparticles, even though gold shells have been fabricated by sequential reverse micelle method.\textsuperscript{44,45} In addition, the magnetoresistance property was explored in this system and magnetoresistance was obtained at 10 K. The displacement reaction method was further examined with Fe nanoparticles. The core-shell structure was not obtained by the Cu
displacement method. Therefore, alternative shells of carbon were investigated with Fe nanoparticles.

The dissertation is presented as follows. In Chapter 2, fabrication of cobalt nanoparticles and the annealing effect on the nanoparticle and the surfactant are presented; Chapter 3 introduces the displacement reaction method in aqueous solution to fabricate the Co-Cu core-shell nanoparticles, its stability and magnetoresistance; a further study in the displacement reaction with cobalt nanoparticles and gold ions in organic solution for the fabrication of Co-Au core-shell nanoparticles is given in Chapter 4; the annealing effect on the Co-Au core-shell nanoparticle and its magnetoresistance study is also presented in Chapter 4; Chapter 5 describes the displacement reaction of iron nanoparticles with an aqueous copper electrolyte solution; Chapter 6 demonstrates the FeCo alloyed nanoparticle fabrication, the effect of annealing and the displacement reaction with the copper ions; Chapter 7 presents the insulating materials such as PMMA and carbon in protecting the metallic nanoparticles; and the conclusion, preliminary model summary and future work will be presented in Chapter 8.

References


CHAPTER 2 SYNTHESIS AND CHARACTERIZATION OF COBALT NANOPARTICLES AND ANNEALING INVESTIGATION

Cobalt nanoparticles have been investigated for decades due to their potential applications such as in ultrahigh density magnetic recording media.\textsuperscript{1-11} Their physicochemical properties are known to depend on the size, and crystal structure (fcc, hcp and \(\epsilon\)-phase) which in turn is influenced by the synthesis method and further treatment.\textsuperscript{12-16} Face-centered cubic, fcc, (at higher temperatures) and hexagonal close-packed, hcp, (below 425 \(^\circ\)C) crystal structures have long been known for bulk elemental cobalt, however, for nanoparticles, the fcc structure is preferred at low temperatures.\textsuperscript{14} Low temperature wet chemical methods often yield exclusively a single cobalt phase.\textsuperscript{12} Routes for wet chemical synthesis of cobalt nanoparticles can be classified under two categories – solution phase metal salt reduction and metal carbonyl pyrolysis.\textsuperscript{17-20} The third phase (\(\epsilon\), epsilon) was also obtained by wet chemical methods,\textsuperscript{12,13} in which cobalt salts were reduced by lithium triethyl borohydrides (superhydride) in the presence of alkylphosphanes as a stabilizer\textsuperscript{13} and thermal decomposition of octacarbonyldicobalt in the presence of trioctylphosphine oxide (TOPO) as a stabilizer.\textsuperscript{12}

Stabilizing surfactants are required in the wet chemical nanoparticle synthesis process as they can prevent agglomeration, control the crystal (phase) growth and shape by selectively binding onto different crystal surfaces,\textsuperscript{12} influence the solubility in different solvent systems and participate in the formation of intermediate states in early stages of the reaction,\textsuperscript{21-23} and affect the magnetic properties\textsuperscript{24} and electronic structure\textsuperscript{25-28} of the nanoparticles. Most commonly used weak or non-polar surfactants, such as oleic acid leading to the formation of oil soluble cobalt colloids,\textsuperscript{29-34} and polar solvents for the
fabrication of polar solvent soluble cobalt nanoparticles were demonstrated. The effect of the surfactant (oleic and lauric acid) on the morphology and self-organization of hcp-phase cobalt nanoparticles was reported. Zwitter ionic surfactants such as lauryl sulfobetaine, have been recently used to stabilized cobalt nanoparticles. This surfactant is used here and the effect of the annealing process on the cobalt nanoparticle morphology and properties is reported.

X-ray absorption near edge structure (XANES) is a very sensitive tool to investigate the electronic structure (i.e., oxidation state and effective charge) of the absorbing atom, the coordination geometries, and different bonding types. By comparing the measured spectra of the substance under investigation to the spectra of well characterized standard reference samples, known as XANES fingerprinting, information on the electronic and geometric properties can be provided. It is also very instructive to compare the XANES spectra with the theoretical spectrum calculated by the real space Green’s function code FEFF8. For sulfur-containing organic analysis, XANES is a nondestructive tool, and the successful application of inspecting the sulfur K-edge XANES fingerprint has been demonstrated in complex molecules, rubber, and biological samples. In this study, the calculated spectra for the Co K-edge XANES were used to support the observed phase structures and the sulfur K-edge XANES was used to verify the valence state of the surfactant after annealing process.

2.1 Synthesis and Annealing Study of the Cobalt Nanoparticles

The synthetic route developed for sulfobetaine stabilized Co nanoparticles is as follows: dodecyldimethyl(3-sulfopropyl)ammonium-hydroxide (SB3-12, 0.015 mol) and 15 ml superhydride (lithium hydrotriethyl borate, 1 M superhydride tetrahydrofuran (THF)
solution, 0.015 mol) were mixed together in 100 ml THF to obtain a clear solution. The above solution was added drop by drop to the solution of CoCl$_2$ (0.0285 mol) in 100 ml THF solvent within a half hour under ultrasonication and nitrogen protecting conditions. The reaction was continued for one more hour. The solution was quenched by adding ethanol and the precipitated cobalt nanoparticles were washed thoroughly with THF and dried under vacuum at room temperature. The powder could be re-dissolved in ethanol, THF or water to obtain a stable colloid. The annealing process was done in a quartz tube with nitrogen protection at a flow rate at 500 standard cubic centimeters per minute (sccm) for 2 hours and cooled naturally in a tubular furnace.

2.2 Characterization

Transmission electron microscopy (TEM) measurements were performed on a JEOL 2010 microscope with an accelerating voltage of 200 kV. For TEM observation, the nanoparticles were dispersed in tetrahydrofuran and then deposited on an amorphous holey carbon coated copper grid. Co weight content in the cobalt nanoparticle complex was analyzed by atomic absorption spectroscopy elemental analysis (measured at the CHN lab, Chemistry Department at University of Michigan Ann Arbor). Thermal analysis was carried out using a differential scanning calorimeter-thermogravimetric analyzer (DSC-TGA) (TA Instruments, SDT 2960) under nitrogen flow at a rate of 50 sccm. The heating rate used was 5 °C per minute. Fourier transform infrared spectroscopy (FT-IR) was used to test the effect of different functional groups of the surfactant on the nanoparticle and was conducted in the Thermo Nicolet Nexus 670 FT-IR spectrometer with transmission mode. The pure surfactants were ground with KBr and compressed into a pellet, their spectra were recorded as a reference spectrum to be compared with those of the fresh and
annealed cobalt nanoparticle spectra. X-ray diffraction experiments were carried out using the CPS120 Inel curved position sensitive detector utilizing Co Kα radiation (measured at MSTD-CMS at Lawrence Livermore National Laboratory, Livermroe, CA). The samples were loaded onto a special sealed aluminum container with a kapton film window for the x-ray probe.

Cobalt K-edge and sulfur K-edge XANES spectra were collected at the DCM beamline at the 1.3 GeV electron storage ring of the Center for Advanced Microstructures and Devices (CAMD) synchrotron radiation facility at Louisiana State University. The experiments were performed in standard transmission mode using ionization chambers filled with nitrogen at 1 atmospheric pressure at Co K-edge and S K-edge. The monochromator was equipped with Si (311) crystals, and the photon energy was calibrated relative to the absorption spectrum of a standard 7.5 µm cobalt foil setting the first inflection point at 7709 eV for the cobalt spectra and was calibrated relative to the absorption spectrum of ZnSO₄ setting the first inflection point at 2481 eV for the sulfur spectra. Standard XANES data analysis was performed using the WINXAS97 software package, where raw spectra were normalized and the background corrected by fitting the pre-edge region with a straight line, and the post-edge region with a third order polynomial. Samples for XAS measurements were prepared by spreading a thin layer of the dried particles uniformly over the Kapton® tape in a glove box with nitrogen protection and transferred to the beam with a sealed holder under nitrogen protection to prevent cobalt nanoparticle oxidation.

Magnetic studies were carried out using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S). The temperature dependent
magnetization was measured in an applied field of 100 G between 4 K and 300 K using zero-field-cooled (ZFC) and field cooled (FC) procedures. The field dependent magnetization was measured at 10 K and 300 K. The cobalt nanoparticle sample were placed in the gelatin capsules in powder form in a nitrogen-protecting glove-box before being inserted in the sample space of the magnetometer to reduce the possible oxidation of the cobalt nanoparticles.

2.3 Results and Discussion

The sulfobetaine surfactant used in this study, 3-(N,N-dimethyldodecylammonium)-propanesulfonate (SB3-12), like other surfactants, protects the colloidal cobalt nanoparticles from agglomeration in the solution due to the balance between electrostatic, magnetic and the Van der Waals force. Superhydrides used in the synthesis were found to be superior to other metal borohydrides due to the the absence of boronmetallic products. After adding a superhydride reducing agent to the cobalt chloride solution, the blue solution changed to black indicating the formation of the colloidal cobalt nanoparticles. The dried nanoparticle powder could be re-dissolved in ethanol, THF or water indicating that sulfobetaine bound to the cobalt nanoparticles is responsible for the solubility in these polar solvents.

Figure 2.1 shows TEM bright field micrographs and electron diffraction patterns of the fresh cobalt nanoparticles, and two annealed cobalt nanoparticles. The fresh cobalt nanoparticles are well dispersed, with a diameter of 3.1 nm ± 0.5 nm. The spacing distance (2.1 Å) of the lattice fringes can be assigned to (111) of fcc cobalt. The existence of the lattice fringe in the fresh nanoparticles indicates the crystalline rather than amorphous structure. The selected area electron diffraction patterns show fcc structure with some
cobalt oxide impurities. The cobalt nanoparticles annealed at 250 °C for 2 hours show increased particle size of 22.3 nm ± 8.3 nm and a combination of fcc and hcp phase structure. The spacing distance (2.15 Å) of the lattice fringes can be assigned either to (111) fcc cobalt or (100) hcp cobalt. The cobalt nanoparticles annealed at 450 °C for 2 hours show the further increase in the particle size of 24 nm ± 6 nm and a phase change from the fcc to hcp structure. The existence of the cobalt oxide impurities in all the three samples could be due to the exposure of samples to air during the TEM sample preparation and transportation of the sample to the TEM instrument. The difference in the electron diffraction patterns (from rings to spots as shown in Figure 2.1 (b), (d) and (f)) of the three samples indicates that the annealing process renders cobalt nanoparticles more crystalline. In addition, the innermost ring with a lattice spacing of 3.34 Å in Figure 2.1 (d) and (f) corresponds to (002) carbon, which indicates that the annealing process leads to the thermal decomposition of the surfactant. Due to the small difference in the rings and spots among the annealed samples and the existence of some oxide impurities seen in electron diffraction, the cobalt structure was further analyzed by XRD and Co K-edge XANES, in which the sample preparation and the measurements were conducted in an inert-gas atmosphere. Table 2.1 shows the elemental analysis by energy dispersive analysis (EDAX) in TEM for the three samples. The relative percentage of elemental sulfur as compared with cobalt was found to increase after annealing, which indicates that the surfactant coated on the cobalt nanoparticles has changed. The sulfur valence state was determined by the sulfur K-edge XANES and the cobalt valence state and crystal structure were investigated by XRD and Co K-edge XANES.
Figure 2.1 (a) (c) and (e) TEM bright field micrograph; and (b) (d) and (f) electron diffraction of (a,b) fresh cobalt nanoparticles, and annealed at (c,d) 250 °C and (e,f) 450 °C.
Table 2.1 EDAX elemental analysis of the cobalt nanoparticles

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sulfur atomic percentage</th>
<th>Cobalt atomic percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh Co nanoparticles</td>
<td>0.8</td>
<td>99.2</td>
</tr>
<tr>
<td>Co NPs annealed at 250 °C</td>
<td>7.5</td>
<td>92.5</td>
</tr>
<tr>
<td>Co NPs annealed at 450 °C</td>
<td>27.6</td>
<td>72.4</td>
</tr>
</tbody>
</table>

Figure 2.2 shows the XRD patterns of the fresh, and two annealed cobalt nanoparticles. The broadened peaks are characteristic of the nanoscale size. The fresh Co nanoparticles have a peak at 52.44 ° with a calculated lattice spacing of 2.03 Å, which is assigned to (111) typical of the fcc cobalt structure. The cobalt nanoparticles annealed at 250 °C show a combination of fcc and hcp structure. The peaks of 49.83 °, 52.56 °, 55.95 ° and 91.38 ° as shown in Figure 2.2 with a lattice spacing of 2.11 Å, 2.04 Å, 1.90 Å, and 1.25 Å are assigned to hcp cobalt phase (100), (002), (101) and (110), respectively. The peak at 52.10 ° with a lattice spacing of 2.04 Å can be assigned to fcc (111). The nanoparticles annealed at 450 °C show a peak at 72.87 ° with a lattice spacing of 1.50 Å assigned to hcp cobalt (102) as well as the other typical hcp peaks seen in the sample annealed at 250 °C. The stronger (102) reflection as compared with other peaks indicates that the annealing process favors nanoparticle re-crystallization in this direction.

The cobalt nanoparticle size was calculated based on Scherrer's equation, \(0.9\lambda/\beta\cos\theta\), where \(\lambda\) is the radiation resource wavelength, \(\beta\) is the full-width at half maximum of the peak, and \(\theta\) is the peak location. The size of the particles in the fresh sample determined from (111) peak is about 8.5 nm. The size of the particles in the two annealed samples was found to be about 65 nm from (110) peak, and 72 nm from (102) peak for the samples annealed at 250 °C and 450 °C, respectively. The calculated particle
sizes are in the same magnitude and slightly larger than those observed from the TEM measurements. The larger size in XRD is due to a different sample preparation than in the TEM sample preparation. XRD samples were dried and pressed while the TEM nanoparticle samples were dispersed in solution. In addition, the limitation of XRD analysis in nanoparticle examination is that the signal is more sensitive to the larger size particles than the smaller ones. Therefore, the calculated size from the XRD signal is not an average of the sample but weighted towards the larger size particles. The particle size from TEM is a more straightforward average.

Figure 2.2 X-ray diffraction patterns of freshly prepared Co nanoparticles, Co nanoparticles annealed at 250 °C and annealed at 450 °C, respectively. (Italic numbers indicates the hcp structure, the others indicate the fcc structure, the two dotted lines indicate the cobalt oxide line)
XANES is a very sensitive tool to study the geometric and electronic structure of the solid material even for small size particles and non-crystalline samples, as compared with the XRD method which requires the sample to be crystalline and of larger size. Figure 2.3(a) shows Co K-edge XANES spectra of the standard hcp Co foil, Co nanoparticles prepared in a glove-box with nitrogen protection, and two standard cobalt oxides (CoO and Co$_2$O$_3$) as reference. The XANES spectrum of the Co nanoparticles is similar to the standard Co foil. The spectrum exhibits a pre-edge feature at approximately 7709 eV, assigned to an electron transition from 1s to a hybridized p-d orbital, and a white line at about 7724 eV. The position of the absorption edge in the cobalt nanoparticle spectrum, as well as the intensity, and the energy location of the maximum white line closely resemble the standard Co foil. The chemical shift of the absorption edge to higher energies (7728 eV), lower pre-edge intensity and a higher energy white line evident in the spectra of the standard CoO and Co$_2$O$_3$ samples were not observed in the Co nanoparticles. These observations indicate that the cobalt nanoparticles prepared in the nitrogen-protected glove-box are not oxidized. In addition, the spectrum of the cobalt nanoparticles differ from the hcp foil which indicates that the crystal structure (phase) of the nanoparticles is different from the standard hcp Co.

The phase structures of the fresh and two annealed Co nanoparticles were further analyzed by comparing the spectrum features of the theoretical spectra of the fcc, hcp and epsilon phase cobalt. Figure 2.3(b) shows the theoretically predicted hcp, fcc and epsilon cobalt spectra using the FEFF8 code. After comparison of the spectrum resonances for the three theoretical phase spectra, some dramatic differences were observed in the white line region. Hcp and fcc structures are different from the epsilon phase in that the latter has
only one peak in the white line energy region (7725-7740 eV), while the first two phases have two well resolved peaks in these regions. The difference between the fcc and hcp phase structure is the relative intensity of these two peaks. Combining with the intensity of the pre-edge shoulder and the chemical shift, this feature, which is common in the series of 3d transition metal K-edge spectra of bulk metals, can be assigned to a pd-hybridization and can be used as a sensitive indicator for the dominant presence of a pure metallic phase of a pure metal.

Figure 2.3 (c) shows the spectra of cobalt foil, fresh cobalt nanoparticle, and two annealed Co nanoparticles. The zero-valence state cobalt nanoparticles for the two annealed samples were also confirmed by the absence of the chemical shift in the edge position. This indicates that the amount of cobalt oxide impurities in the annealed cobalt nanoparticles is negligible even though the bounded surfactant appears to decompose at high temperature during the annealing process. Further comparison of the intensity of the two peaks at about 7727 and 7733 eV provides information about the phase structure of the cobalt nanoparticles. In the fresh nanoparticle spectrum, the amplitude of the first peak in the double-peak white line region is higher than that of the second peak, while for the spectrum of the nanoparticle annealed at 450 °C the reverse is true. This observation indicates that fresh nanoparticles possess fcc phase structure and the nanoparticles annealed at 450 °C mostly have hcp structure. As to the sample annealed at 250 °C, the difference in the intensities of the two peaks almost disappears and, unlike the characteristic of only epsilon phase cobalt in the white line as shown in Figure 2.3 (b), this indicates that a combination of the fcc and hcp phase structure is present.
Figure 2.3 XANES spectra of the (a) hcp cobalt foil, fresh cobalt nanoparticles, standard CoO and Co$_2$O$_3$ as reference; (b) simulated hcp, fcc and epsilon Co; (c) standard hcp Co foil, as-synthesized Co nanoparticles, annealed at 250 °C and 450 °C cobalt nanoparticles (inset shows the enlargement of the white line peaks).

It has been reported that the particle size may have a major effect on the cobalt nanoparticle crystal structures. Particles with size less than 20 nm are found to be fcc phase, whereas particles larger than 40 nm prefer the hcp phase. The explanation of the
phase was based on the particle total free energy.\textsuperscript{14} Combining analysis from XRD and XANES, a predominant fcc phase was observed for the fresh samples. A combination of fcc and hcp phase was found for the cobalt nanoparticle annealed at 250 °C for 2 hours. The sample annealed at 450 °C for 2 hours is found to have dominant hcp phase. The fcc phase for the fresh sample is consistent with the prediction that small size cobalt nanoparticles with fcc phase are stable.\textsuperscript{60} The observed increase in the cobalt nanoparticle size could contribute to the hcp phase formation after annealing process.

Figure 2.4 shows the weight percentage change with temperature of surfactant, and fresh cobalt nanoparticles as determined by TGA. It was observed that the decomposition temperature of the surfactant is between 200 °C and 300 °C, which is consistent with the recent literature results\textsuperscript{61,62} and also from the reported melting temperature (point. 250-260 °C).

![Figure 2.4 TGA of surfactant bound to cobalt nanoparticles and the unbound, free surfactant](image)

**Figure 2.4** TGA of surfactant bound to cobalt nanoparticles and the unbound, free surfactant
Figure 2.5 FT-IR spectra of the SB3-12, SB3-12 stabilized cobalt nanoparticles, SB3-12 stabilized cobalt nanoparticles annealed at 250 °C and 450 °C, respectively.

The FT-IR spectra of the surfactant, fresh cobalt nanoparticle and annealed cobalt nanoparticles are shown in Figure 2.5. Overall, the spectrum of the surfactant on the surface of the fresh nanoparticles is similar to that of the free surfactant. The strong bands at 2919 and 2851 cm\(^{-1}\) are assigned to the asymmetric and symmetric CH\(_2\) stretching modes, respectively.\(^{39}\) These two peaks are almost the same between the bound and unbound surfactant except for the narrowing of the peaks in the case of surfactant bounded to the cobalt nanoparticles, which is attributed to the immobilization of the surfactant molecules on the particle surfaces.\(^{39,63}\) The first peak at 1488 cm\(^{-1}\) is due to the asymmetric mode of the CH\(_3\)-(N\(^+\)) group, and the second at 1468 cm\(^{-1}\) is assigned to the CH\(_2\) scissoring mode.\(^{64,65}\) These two peaks are shifted to lower wavenumbers when the surfactant is coated on the cobalt nanoparticles, suggesting a less mobile environment, and a strong association
of these functional groups on the surface of the cobalt nanoparticle. This indicates that the quaternary ammonium group coordinates to the surface of the cobalt nanoparticle and protects the cobalt nanoparticle from agglomeration. The symmetric stretching mode of the S-O is observed as a bimodal broad band around 1275 and 1150 cm\(^{-1}\). The narrowing of these peaks for the surfactant bounded to the cobalt nanoparticles indicates the relatively lower mobility of these functional groups in the coated cobalt nanoparticle samples. After annealing the cobalt nanoparticles at 250 °C and 450 °C for 2 hours, the obvious disappearance of the characteristic peaks was observed indicating the decomposition of the SB3-12.

The effect of annealing on the surfactant bounded cobalt nanoparticle system was further studied by the sulfur K-edge XANES. Figure 2.6 shows the S K-edge XANES of the fresh cobalt nanoparticles, two annealed cobalt nanoparticle and the free surfactant as reference. The first inflection point for the surfactant bounded to the cobalt nanoparticle is 2480.0 eV similar to the free surfactant and a typical characteristic of the +6 sulfur compounds such as potassium sulfate.\(^6\) The second inflection point at 2485.2 eV shifts toward lower energy as compared with the surfactant. The intensity of the white line in surfactant bounded to cobalt nanoparticles is much stronger than the free surfactant. The increased intensity and the shift of the second inflection point indicate an existence of a strong bonding between the surfactant and the cobalt nanoparticle surface. After the annealing process, the first inflection point for the +6 sulfur was decreased and new inflection points (2470.3 eV and 2477.2 eV can be assigned to +2 and +4 sulfur species) appear indicating the formation of intermediate materials as a consequence of the surfactant decomposition, which is consistent with the electron diffraction observation of
the carbon formation. After a higher temperature (450 °C) annealing process, the disappearance of the +6 sulfur inflection point indicates complete decomposition of surfactant, which is consistent with the FT-IR analysis result.

Figure 2.6 Sulfur XANES spectra of the surfactant, fresh cobalt nanoparticles, cobalt nanoparticles annealed at 250 °C and 450 °C.

Figure 2.7 shows the field dependent magnetization of the fresh, Figure 2.7 (a), and the annealed Co nanoparticles at 250 °C Figure 2.7 (b), and 450 °C Figure 2.7 (c), measured at 10 and 300 K. Table 2.2 summarizes the magnetic parameters. It was observed that the coercivity (the field required for the magnetization to be zero) and the remanent magnetization (the magnetization when the field was zero) are nonzero at 10 and 300 K for the fresh and the annealed samples indicating the ferromagnetic property of the cobalt
nanoparticles, which is consistent with the blocking temperature (the temperature, at which the superparamagnetic state transits to a ferromagnetic state) determined from the zero field cooled and field cooled temperature dependent magnetization. The increase of the saturation (Ms) and remanent magnetization (Mr) after the annealing process is attributed to the increased size and more crystalline structure of the nanoparticles. However, the saturation magnetization of the cobalt nanoparticles annealed at 450 °C (143.8 emu/g) is still lower than the bulk cobalt (162 emu/g) indicating that there is a strong interaction between the sulfobetaine and the cobalt atoms in the surface as reported for cobalt nanoparticles stabilized by other surfactants.  

Figure 2.7 Hysteresis loops of (a) fresh Co nanoparticles at 10 K and 300 K; (fig. continued)
Figure 2.7 (Continued) (b) Co nanoparticles annealed at 250 °C; (c) Co nanoparticles annealed at 450 °C (right-bottom insets are the enlargement at low field.)
Table 2.2 Magnetic data for cobalt nanoparticles

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (K)</th>
<th>Hc (Oe)</th>
<th>Ms (emu/g Co)</th>
<th>Mr (emu/g Co)</th>
<th>Mr/Ms</th>
<th>M from ZFC (emu/g)</th>
<th>m (µB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh Co NPs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>347</td>
<td>32.7</td>
<td>3.5</td>
<td>0.11</td>
<td>0.92</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>17</td>
<td>12.0</td>
<td>0.06</td>
<td>0.02</td>
<td>1.19</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>250 °C annealed NPs</td>
<td>10</td>
<td>475</td>
<td>91.6</td>
<td>28.4</td>
<td>0.31</td>
<td>2.65</td>
<td>0.19</td>
</tr>
<tr>
<td>300</td>
<td>272</td>
<td>88.5</td>
<td>24.6</td>
<td>0.28</td>
<td>4.34</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>450 °C annealed NPs</td>
<td>10</td>
<td>660</td>
<td>150.1</td>
<td>43.8</td>
<td>0.29</td>
<td>3.41</td>
<td>0.22</td>
</tr>
<tr>
<td>300</td>
<td>328</td>
<td>143.8</td>
<td>33.7</td>
<td>0.23</td>
<td>6.04</td>
<td>1.57</td>
<td></td>
</tr>
</tbody>
</table>

* Ms was calculated from the intercept of the M vs. 1/H at high field.

The ratio of the remanent magnetization to the saturation magnetization (Mr/Ms), also called squareness, for the two annealed samples increase compared with the fresh sample; this is attributed to the defects in the crystalline structure, surface effects as well as the particle size distribution and phase transition from fcc to hcp. Cobalt nanoparticles annealed at 450 °C have a lower ratio of remanent to saturation magnetization as compared with the cobalt nanoparticles annealed at 250 °C; this is attributed to the phase transition from fcc+hcp to hcp structure. The observation is consistent with a recent report that fcc cobalt has higher ratio (0.8) of remanent to saturation magnetization than hcp cobalt (0.5). The observed lower ratio of the remanent to the saturation magnetization for the fresh and annealed cobalt nanoparticles compared to the reported ratio arises from the surface effects due to the different surfactant system. The increase of the coercivity arises from the phase transition after the annealing process. It is known that coercivity is proportional to the anisotropy energy, K, (Hc=2K/Ms) in single domain nanoparticles.
The hcp phase cobalt has much higher anisotropy (K=4.5×10^6 erg/cc) than the fcc phase cobalt (K=5×10^5 erg/cc). With the increase of the annealing temperature, fcc phase changed from the mixture of hcp+fcc to pure hcp, thus increased the coercivity.

The magnetic moment, $m$, of the particle was calculated based on the equation, $m = 2.83\sqrt{T\chi}$, \[^{70,71}\] with a unit of $\mu_B$, where $\chi$ is the mole susceptibility with a unit of emu/mole, and $T$ is the temperature with a unit of K. The mole susceptibility was determined by the magnetization (emu per mass cobalt) divided by the cobalt atomic weight. The magnetization (emu/g particle) was read from the zero field cooled (ZFC) temperature dependent magnetization curve (shown in Table 2.2) and was determined by considering the cobalt content (analysis by atomic absorption) and assuming bulk cobalt density (8900 kg/m\(^3\)). After the cobalt weight conversion (cobalt weight percentage was 44.3\%, 53.3\% and 45.9\% for the fresh cobalt nanoparticles, nanoparticles annealed at 250 °C and annealed at 450 °C, respectively), the calculated magnetic moment for the fresh, annealed at 250 °C and 450 °C is 0.11 $\mu_B$ (0.70 $\mu_B$), 0.19 $\mu_B$ (1.33 $\mu_B$) and 0.22 $\mu_B$ (1.57 $\mu_B$) at 10 K (300 K), respectively. It was observed that the annealing process improves the magnetic moment. This is due to the increased size, the more crystalline structure and the phase change to hcp. The dependence of the magnetic moment on the temperature was also observed at the zero-field cooled measurement process as shown in Table 2.2, the higher the temperature, the higher the magnetic moment.

2.4 Summary

The sulfobetaine stabilized cobalt nanoparticles were found to have fcc phase structure and form stable colloids in polar solvents. The protecting surfactant was
chemically bound to the metallic Co core with ammonium functional groups coordinating to the cobalt nanoparticle surface as seen from FT-IR and TGA analysis. XRD and Co K-edge XANES reveals that the cobalt underwent the phase transition from fcc to fcc+hcp and to hcp before and after the annealing process. The annealing process also led to the decomposition of the surfactant as seen by the electron diffraction and sulfur K-edge XANES. The annealing process significantly enhanced the effect on the magnetic properties, as expected for a phase transition from fcc to hcp cobalt.

2.5 References


54 A. Prange, N. Kuhlsen, B. Birzele, I. Arzberger, J. Hormes, S. Antes, and P. Kohler, European Food Research and Technology 212, 570-575 (2001).


V. G. Palshin, R. Tittsworth, J. Hormes, E. I. Meletis, X. Nie, J. Jiang, and H. Modrow, From the Atomic to The Nano-Scale (Old Dominion University, Old Dominion University, 2003).


J. Umemura, D. G. Cameron, and H. H. Mantsch, Biochimica et Biophysica Acta 602, 32-44 (1980).


CHAPTER 3 DISPLACEMENT SYNTHESIS OF COPPER SHELLS 
SURROUNDING COBALT NANOPARTICLES

Iron-group metallic nanoparticles (NPs), cobalt,$^{1-13}$ iron,$^{2,14-16}$ and nickel,$^{2,16,17}$ are of interest due to their unusual magnetic properties, such as an enhanced coercivity compared to thin films or microsize particles.$^{1,18}$ Platinum alloys of Co and Fe nanoparticles have gained recent attention in high density data storage, due to their inherent high magnetic anisotropy.$^{19-29}$ In addition, nanoparticles have been synthesized with alloys of the iron-group elements themselves, including for example FeCo,$^{30}$ CoNi,$^{31}$ and CoNiB.$^{32}$ A common challenge in all these examples is the control of surface properties, since iron-group nanoparticles readily oxidize in air, which requires that the nanoparticles be stored in a protective air environment, such as N$_2$. Cobalt oxide formation is not necessarily deleterious if the oxide shell is stabilized. For example, Co nanoparticles embedded and dispersed in a CoO matrix$^{33}$ results in an increase in the blocking temperature close to room temperature compared to uncoated Co nanoparticles. The blocking temperature represents the point where thermally assisted hopping between different magnetic orientations is blocked and defines the temperature limit where useful ferromagnetic devices can operate. While a favorable increase in coercivity occurs when a ferromagnetic particle decreases to the nanometer range, its blocking temperature unfortunately decreases, unless it is encapsulated. For example, carbon coated iron, cobalt and nickel nanoparticles$^{34}$ and CoPt nanoparticles in poly(methylmethacrylate)$^{35}$ showed blocking temperatures well above room temperature.

In an effort to control the surface chemistry of nanoparticles, the fabrication of a compact noble shell, such as gold,$^{36-40}$ platinum,$^{41,42}$ or silver$^{43,44}$ around the vulnerable
nanoparticle has been demonstrated. The core-shell synthetic methods were discussed in Chapter 1.

In this Chapter, a displacement method is presented to generate copper shells surrounding Co nanoparticles in aqueous solution at room temperature. To the authors’ knowledge, it is the first demonstration of a copper shell around an iron-group element nanoparticle. The exchange reaction takes place in an acid copper-citrate electrolyte$^{45}$ where cobalt oxides are not stable.$^{46}$ The process eliminates the need for strict N$_2$ control after the nanoparticle synthesis. Cobalt oxides can straightforwardly be distinguished with synchrotron XANES (X-ray Absorption Near Edge Structure) techniques, and data showing the absence of oxides in the resulting Co-Cu nanoparticles are presented here. In addition, Cu and Co should have limited miscibility, as suggested by thermodynamic data,$^{47}$ which supports the motive for the Cu shell, however, nonequilibrium phases of CoCu can occur as found in electrodeposited CoCu alloys.$^{48-50}$

3.1 Synthesis of Copper Shell Surrounding Cobalt Nanoparticles

Synthesis of cobalt nanoparticles follows the procedures that were described in Chapter 2. The shell formation occurs by the displacement reaction, at an appropriate pH, where Co(OH)$_2$, the hydrated form of CoO, is not stable. Figure 3.1 is the Pourbaix diagram of the copper-water system. It is a plot of stable phases at different pH values. The lines represent the equilibrium between two phases in a reaction at a particular ion concentration. From the graph, the equilibrium between Co and Co(II) ions (10$^{-6}$ M) occurs at a pH lower than 6.0. Since it is below the region where the oxides are not stable, Co(s) will dissolve in solution. The Co nanoparticles will react with either protons or copper ions according to equations: $Co_{NP} + H^+ \Rightarrow Co^{2+} + H_2 \uparrow$
and $Co_{NP} + Cu^{2+} \Rightarrow Co_{core}Cu_{shell} + Co^{2+}$. In order to favor the copper shell formation, the electrolyte should not be acidic. Here, pH=4 was chosen as a compromise to favor the cobalt-copper reaction while minimizing the cobalt-proton reaction, and avoiding the formation cobalt oxides, that occur spontaneously at high pH.

Figure 3.1 Pourbaix diagram of Co system\cite{46}
The cobalt nanoparticles were added to a copper-citrate electrolyte, containing 0.25 M CuSO$_4\cdot5$H$_2$O, 0.3 M C$_6$H$_5$Na$_3$O$_7\cdot2$H$_2$O, at a pH of 4.0 (measured with pH meter an Orion Thermo model 420, pH was adjusted with concentrated sulfuric acid or sodium hydroxide). The reactants were agitated ultrasonically for 1 hour under atmospheric conditions. The particles were removed from the electrolyte by precipitation and washed thoroughly with de-ionized water. The particles were then dried under nitrogen flow. The color change as shown in Figure 3.2 indicates the formation of a copper shell.

![Figure 3.2 Co and Co-Cu core-shell nanoparticles after being dried](image)

The same technique was adopted to coat cobalt microparticles. Cobalt microparticles (7.162 g) were added to 100 ml cupric-sulfate and sodium citrate electrolyte solution (0.25 M CuSO$_4\cdot5$H$_2$O and 0.3 M C$_6$H$_5$Na$_3$O$_7\cdot2$H$_2$O) with a pH value adjusted to 4.0 and the reactants were agitated ultrasonically throughout the reaction period of 1 hour. After the reaction, the particles changed from gray to copper color, which is an indicator for the formation of the copper shell around the cobalt core particles. Deareated de-ionized water was used to wash thoroughly the precipitated particles until no blue color was observed in the supernatant. The particles were finally dried under nitrogen flow at room temperature and preserved as powder in a glove box for further analysis.
3. 2 Characterization

Nanoparticles were characterized by transmission electron microscopy (TEM) operated on JEOL 2010 with a 200 kV accelerating voltage, UV/vis spectrophotometer and X-ray absorption spectroscopy (XAS). Elemental analysis of the cobalt-copper core-shell was analyzed by atomic absorption analysis (AAA). TEM samples were prepared by dropping a tetrahydrofuran solution of cobalt and an aqueous solution of Co-Cu nanoparticles onto an amorphous holey carbon coated copper and gold grid, respectively. Microscopic examination of the microparticles was carried out using a Cambridge S-260 scanning electron microscope (SEM). X-ray diffraction (XRD) was carried out using the CPS120 Inel curved position sensitive detector system utilizing Co Kα radiation source (measured at Lawrence Livermore National Laboratory, Livermore, CA). The powder samples for XRD were loaded into a sealed aluminum container with a kapton film window. UV/vis spectra were recorded in a 1 cm width cuvette at room temperature using Genesys™ 10 spectrophotometer. Magnetization measurements for all samples were conducted using a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer. The samples for magnetic measurements were prepared in powder form in gelation capsules under inert atmosphere. The temperature dependent magnetization was measured using zero-field-cooled (ZFC) and field-cooling (FC) in an applied magnetic field of 100 G between 4 and 300 K. ZFC was done by cooling the sample first to 4 K without a field; then magnetization changes were recorded with the temperature increasing from 4 to 300 K at an applied field of 100 G. FC was recorded immediately after ZFC by decreasing the temperature from 300 K to 4 K with a constant field of 100 G. Field dependent magnetization (hysteresis loop) was measured at 10 K and
300 K, respectively. The oxidative stability of the cobalt core was studied by cooling the sample from 300 K to 10 K with an applied field of 5 Tesla and then recording the field dependence magnetization at 10 K.

X-ray absorption spectroscopic (XAS) experiments were performed at the XMP double crystal monochromator beamline at port 5A of the Center for Advanced Microstructures and Devices (CAMD) synchrotron radiation source at Louisiana State University, as described in Chapter 1. Samples for XAS measurement were prepared by spreading a thin layer of the dried particles uniformly over Kapton® tape in air for Co-Cu nanoparticles and in a glove box for Co nanoparticles.

The electrochemical reaction rates were characterized on a rotating disk electrode (RDE) using linear sweep voltammetry, (Solartron SI1287 and 1255B). The electrode disk area was 0.283 cm² and the rotation rate was 400 rpm. A Cu disk working electrode was used to characterize the kinetic range of the Cu reduction reaction and a Co disk, working electrode was used to characterize the anodization of Co. The counter electrode was Cu during the Cu reduction study, and Pt during the Co anodization case. The applied sweep rate was 5 mV/s.

Magnetic field dependent resistance was measured with a 9-Tesla Quantum Design PPMS measurement system using the standard 4-probe ac technique as shown in Figure 3.3 and GMR was calculated by $\Delta R / R(0) = \left( [R(H) - R(0)] / R(0) \right) \times 100\%$, where $R(H)$ and $R(0)$ are the resistance at zero and any applied field of H, respectively. The granular structural sample for the GMR measurement was prepared by the cold-press method. The applied pressure was 5000 Psi (Presser model: Carzer Hydraulic 3912) and the pressing
duration time was 2 minutes. The applied magnetic field is perpendicular to the film, i.e., the applied current.

Figure 3.3 Scheme of the standard 4-probe method to measure GMR

3.3 Results and Discussion

Figure 3.4 shows the characteristic UV/vis absorption spectrum of the synthesized Co-Cu core-shell nanoparticles well dispersed in de-ionized water. The plasmon resonance at 579 nm arising from the excitation of plasmon resonance or interband transitions excitations,\(^{51}\) is consistent with nanosize copper,\(^{52}\) indicative of a copper shell around the cobalt core. It has been reported that the cobalt nanoparticles have no plasmon resonance peak at the UV region.\(^ {53,54}\) The particle shape could also produce the variation of the plasmon resonance peak in the range of 480 nm to 600 nm.\(^ {55,56}\) However, the fabricated Co-Cu core-shell nanoparticles was observed to be spherical by TEM, ruling out the shape effect. A large red shift of the plasmon absorption, when compared with that of the pure
spherical copper nanoparticles (~ 566 nm)\textsuperscript{52,57-59} could be attributed to the presence of a cobalt core and also indicate that almost no free copper nanoparticles were formed in the displacement reaction, which is consistent with the literature report on gold-coated silver nanoparticles,\textsuperscript{60,61} gold coated cobalt nanoparticles,\textsuperscript{62} gold coated $\gamma$-Fe$_2$O$_3$ core-shell nanoparticles\textsuperscript{63} and silver shell around a silica core.\textsuperscript{64} The UV/vis spectra for the microparticles were unavailable due to the quick precipitation in the solution during the measurement.

![UV/vis spectrum of Co-Cu nanoparticle in de-ionized water](image)

**Figure 3.4** UV/vis spectrum of Co-Cu nanoparticle in de-ionized water

Figure 3.5 shows a TEM bright field micrograph of the Co-Cu nanoparticles. The particles are discretely dispersed, having a mean diameter of 3.2 nm with standard deviation of 0.6 nm. The fringes shown in Figure 3.6 have an interplanar distance of 0.18
nm. The lattice parameters of Cu and Co are 0.3615 nm and 0.3544 nm, respectively. Assuming a cubic crystallographic structure, then the measured d-spacing corresponds to a (2 0 0) fcc plane, consistent with a Cu shell. But due to the small difference in the lattice constants between Co and Cu, the measured d-spacing could also represent Co. A contrast difference which can arise from the lattice fragments having different orientations with respect to the electron beam has been reported as a distinguishing criterion for a core-shell structure. However, here the very small difference in atomic number Z does not make the core-shell structure distinguishable by TEM. The SEM image of the Co-Cu microparticles shown in Figure 3.7 reveals the well-dispersed and spherical microparticles, having a mean diameter of 0.93 \( \mu \)m with standard deviation of 0.23 \( \mu \)m.

Figure 3.5 TEM images of Co-Cu nanoparticles
Figure 3.6 High-resolution TEM images of Co-Cu nanoparticles showing a 0.175 nm Cu lattice spacing

Figure 3.7 Scanning electron microscopy images of the Co-Cu microparticles
Figure 3.8 Co K-edge XANES spectra of a hcp cobalt foil, cobalt nanoparticles, Co-Cu nanoparticles, Co nanoparticle oxidized in air, and a CoO and Co$_2$O$_3$ reference. Lines A, B, C, D are the zero-valence Co pre-edge, Co white line, CoO and Co$_2$O$_3$ white line, respectively.

XAS was used to verify, indirectly, that the Co core was protected by the Cu shell. Figure 3.8 shows the XANES Co K-edge spectra of a standard hcp Co foil, Co nanoparticles prepared in a glove-box with nitrogen protection, Co-Cu nanoparticles exposed to air, Co nanoparticles exposed to air and two cobalt oxide standards. The XANES spectrum of Co in the Co-Cu core-shell nanoparticle differs from the cobalt oxide spectra and is similar to the air-protected Co nanoparticle and standard Co foil. The data for the Co foil was shown in Figure 2.3 and is repeated here in Figure 3.8 in order to make
a comparison with the Co-Cu core-shell nanoparticles. The Co XANES spectrum of the 
Co-Cu sample exhibits a pre-edge feature at approximately 7709 eV, (line A) assigned to 
an electron transition from 1s to a hybridized p-d orbital, and a white line at about 7724 eV 
(line B). The position of the absorption edge in the Co-Cu spectrum, as well as the 
intensity, and the energy location of the maximum white line closely resemble the Co 
nanoparticles and the standard hcp Co foil. The chemical shift of the absorption edge to 
higher energies (7728 eV), lower pre-edge intensity and a higher white line (lines C and D) 
evident in the spectra of the CoO and Co$_2$O$_3$ was not observed in the Co-Cu sample, nor 
the N$_2$ protected Co nanoparticle sample. Numerous literature studies have shown that 
when Co nanoparticles are exposed to air they readily oxidize$^{10,12,68-70}$ and this is 
confirmed as well in the XANES spectra in Figure 3.8. Thus, the XANES experiments 
prove that the Cu shell has effectively protected the Co nanoparticle from cobalt oxidation 
formation in air.

Figure 3.9 shows the XRD patterns of pure cobalt nanoparticles, cobalt 
microparticles, the corresponding core-shell Co-Cu particles and an oxidized cobalt (CoO) 
nanoparticle as a reference. The XRD pattern for the cobalt nanoparticles prepared under 
nitrogen protection shows face-centered-cubic (fcc) structure with the typical peak (111) 
for fcc cobalt as shown in Figure 3.9B. For cobalt microparticles, the observed peaks of 
49.55°, 52.84°, 56.61°, 75.06°, and 92.43° as shown in Figure 3.9C with a lattice spacing 
of 2.14 Å, 2.01 Å, 1.89 Å, 1.47 Å and 1.24 Å are assigned to hexagonal-closed-packed 
(hcp) cobalt phase (100), (002), (101) and (110), respectively. Fcc phase cobalt was also 
observed in the cobalt microparticles, peaks 53.03°, 61.68°, and 91.89° with a lattice 
spacing of 2.04 Å, 1.75 Å and 1.25 Å can be assigned to fcc phase (111), (200) and (220),
respectively. The Co-Cu core-shell microparticles show weak hcp cobalt structure with an fcc phase as seen in Figure 3.9F. There is no cobalt oxide signal observed. The weak hcp cobalt signal in the core-shell microparticles and the disappearance of the cobalt signal (Figure 3.9E) altogether in the core-shell nanoparticles indicate that the copper shell prevents the diffraction from the core cobalt. XRD patterns of both the micro and the nano core-shell particles show strong fcc copper reflections with (111), (200) and (220) and no evidence for the existence of copper oxides. The calculated average copper lattice constant (3.619 nm) for the Co-Cu nanoparticles is almost the same as for the Co-Cu microparticles (3.613 nm). The Co-Cu nanoparticles freshly prepared or stored as powder under inert atmospheric conditions did not show any copper oxide impurities as shown in Figure 3.9E, however, the Cu shell of the Co-Cu nanoparticles immersed in oxygenated water for a month under atmospheric conditions, was partially oxidized to Cu₂O as seen in Figure 3.9D with the characteristic peaks of (110), (111), (200) and (220) for Cu₂O.

Figure 3.10 shows the temperature dependent magnetization (normalized to the magnetization at 300 K) of (a) fresh nanoparticles unexposed to air, aged Co-Cu nanoparticles exposed to air for 4 and 7 months curves and freshly prepared cobalt nanoparticle in a paste form, and (b) microparticles (MPs). The blocking temperature, T_B, determined from the maximum of the ZFC curve, indicates the transition from ferromagnetic to superparamagnetic behavior. Compared with Co nanoparticles, without a shell, the T_B is below room temperature (124 K) as expected for nanosize particles. The core-shell Co-Cu nanoparticles show an enhanced T_B (235 K), as seen in Figure 3.10(a). Upon aging, the T_B remains 235 K. Figure 3.10(b) shows that both Co and Co-Cu microparticles exhibit T_B above room temperature, which is attributed to the bulk-like size.
The blocking temperature, $T_B$, was determined from the coercivity at the two temperatures, $T_1$ and $T_2$, according to, $H_C(T_1)/[1-(T_1/T_B)^{2/3}]=H_C(T_2)/[1-(T_2/T_B)^{2/3}]$. A higher $T_B$ (1212 K) was observed for the Co-Cu core-shell microparticles in comparison with Co microparticles (848 K). The larger slope of the normalized FC magnetization curve indicates a weaker inter-particle interaction. Compared with the cobalt particles, the counterpart Co-Cu particles show a slightly stronger particle interaction as can be observed from the normalized FC curves, which was also observed recently in the high density of two-dimensional self-assemblies of cobalt nanoparticle and could be responsible for the increase in the blocking temperature.

![XRD patterns](image)

**Figure 3.9** XRD patterns for (A) cobalt oxide nanoparticles, (B) cobalt nanoparticles, (C) cobalt microparticles, (D) Co-Cu core-shell nanoparticle with partial copper surface oxidation, (E) Co-Cu core-shell nanoparticles, and (F) Co-Cu core-shell microparticles.
Figure 3.10 ZFC and FC magnetization of (a) fresh and aged Co-Cu core-shell nanoparticles, and the fresh Co nanoparticle in a paste form; and (b) microparticles. (Magnetization was normalized at 300 K)
Figure 3.11 ZFC hysteresis loops of (a) Co-Cu core-shell microparticles and (b) Co-Cu core-shell nanoparticles. (Insets: Co particles)
The existence of hysteresis at 300 K for both the Co precursor microparticles and the Co-Cu microparticles, shown in Figure 3.11 (a), is consistent with the high blocking temperature. Similarly, for nanoparticles as shown in Figure 3.11 (b), the hysteresis loop is consistent with the observed $T_B$ for the Co and Co-Cu nanoparticles, as evidenced by the superparamagnetic behavior at 300 K. The coercivity value of the Co-Cu microparticles ($H_c=285$ Oe and 180 Oe at 10 K and 300 K, respectively) compared to the coercivity of the Co microparticles, without the shell ($H_c=330$ Oe and 173 Oe at 10 K and at 300 K, respectively) both increased with a decrease of the measuring temperature, as expected, due to a decrease in thermal effects at lower temperatures. The coercivity was lowered for the microparticles with the Cu shell at 10 K. The coercivity of the nanoparticles showed a reverse trend as compared with the microscopic particle; there is a larger coercivity observed for the core-shell particle. Since the Co nanoparticles are not ferromagnetic at room temperature only the low temperature case can be compared, at 10 K, the coercivity ($H_c$) is 698 Oe for Co-Cu nanoparticles and 656 Oe for Co nanoparticles. The increase of the coercivity with the decrease of the particle size was also observed and is consistent with the results reported elsewhere, see review.\textsuperscript{76}

The presence of cobalt oxide impurities in the core-shell structure due to air exposure can be monitored by shifts in the field cooled (at 5 Tesla) hysteresis loop. If the cobalt core is oxidized, the hysteresis loop will shift toward the applied magnetic field direction due to the exchange-coupling between the ferromagnetic core and the antiferromagnetic oxide shell.\textsuperscript{69,70,77,78} Figure 3.12 shows the field cooled (FC) hysteresis loop for the (a) Co-Cu microparticles and (b) Co-Cu nanoparticles exposed to air for 4 months, and (c) Co-Cu nanoparticles exposed to air for 7 months. Table 3.1 summarizes
the magnetic parameters. The almost overlapping curves of the FC and ZFC hysteresis shows in Figure 3.12 (a) that there is negligible cobalt oxide around the cobalt core in the Co-Cu microparticles after exposure to air during the sample transfer; in Figure 3.12 (b) that there is a negligible amount of cobalt oxide formed even after the Co-Cu nanoparticles were exposed to air for 4 months. The Co-Cu nanoparticles were also aged for 7 months and their magnetic properties are shown in Figure 3.12 (c). A slight change in the coercivity was observed, indicating some cobalt oxide. It was also reported that the existence of the antiferromagnetic layer around the ferromagnetic particle will increase the $T_B$ in the cobalt nanoparticles.\textsuperscript{33} There was no change in $T_B$ for the Co-Cu nanoparticles after aging for a period of 4 and 7 months in air, compared with the fresh sample. Summarized in Figure 3.10 (a) and Table 3.1 there is no significant cobalt oxide formation after a 4-month period exposed to air, and a slight degradation after 7 months.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{hysteresis_loop.png}
\caption{ZFC and FC (with a cooled field of 5 Tesla) hysteresis loops at 10 K for (a) Co-Cu core-shell microparticles (fig. continued)}
\end{figure}
Figure 3.12 (Continued) (b) aged for 4 month Co-Cu core-shell nanoparticles and (c) aged for 7 month Co-Cu core-shell nanoparticles
Table 3.1 Coercivity values of ZFC and FC magnetization field dependence at 10 K

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_B, K</th>
<th>Hc (ZFC), Oe</th>
<th>Hc(FC at 5 Tesla), Oe</th>
<th>Mr/Ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-Cu MPs fresh</td>
<td>1212</td>
<td>-297</td>
<td>-318</td>
<td>0.12</td>
</tr>
<tr>
<td>Co-Cu NPs aged 4 months</td>
<td>235</td>
<td>-706</td>
<td>-839</td>
<td>0.28</td>
</tr>
<tr>
<td>Co-Cu NPs aged 7 months</td>
<td>235</td>
<td>-702</td>
<td>-857</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Table 3.2 Magnetic properties from ZFC temperature dependence magnetization and average cobalt composition in the particles

<table>
<thead>
<tr>
<th>Sample</th>
<th>T(K)</th>
<th>M (emu/g)</th>
<th>Co content (weight)</th>
<th>Susceptibility (10^{-5} emu/mole)</th>
<th>Magnetic moment (µ_B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co NPs</td>
<td>300</td>
<td>0.11</td>
<td>0.0836</td>
<td>22.3</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.04</td>
<td>0.0836</td>
<td>8.12</td>
<td>0.11</td>
</tr>
<tr>
<td>Co-Cu NPs</td>
<td>300</td>
<td>0.26</td>
<td>0.04</td>
<td>110</td>
<td>1.628</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.05</td>
<td>0.04</td>
<td>21.2</td>
<td>0.130</td>
</tr>
<tr>
<td>Co MPs</td>
<td>300</td>
<td>3.75</td>
<td>0.459</td>
<td>139</td>
<td>1.826</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2.72</td>
<td>0.459</td>
<td>101</td>
<td>0.284</td>
</tr>
<tr>
<td>Co-Cu MPs</td>
<td>300</td>
<td>3.19</td>
<td>0.186</td>
<td>291</td>
<td>2.645</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2.33</td>
<td>0.186</td>
<td>213</td>
<td>0.413</td>
</tr>
</tbody>
</table>

The magnetic moment of the particles was calculated following the same procedure as in Chapter 2. The cobalt weight content was characterized by the atomic absorption analysis. Table 3.2 summarizes the magnetic properties for the Co and Co-Cu core-shell particles. The enhanced magnetic moment after the formation of the copper shell around the cobalt core is consistent with the recent theoretical calculated prediction, using a parameterized tight-binding model\textsuperscript{79} and a spin-polarized s-p-d tight-binding model\textsuperscript{80} for
clusters of a cobalt core with a noble metal shell (copper), which develops a net polarization and changes the total magnetic moment of the clusters. The dependence of the magnetic moment on the temperature was also observed at the zero-field cooled measurement process, the higher the temperature, the higher the magnetic moment.

**Figure 3.13** Evans diagram for the cobalt anodization and copper reduction on a RDE at 400 rpm.

The displacement reaction rate was estimated from an Evans diagram, shown in Figure 3.13. The rotation rate was arbitrarily selected so that it was large enough to capture the kinetic regime of both the bulk cobalt anodization in a copper-free electrolyte and the
copper reduction from a copper electrolyte. The mixed potential corrosion current thus represents an upper limit on the reaction rate. Mass transport limitations would lower this value. Due to the ultrasonic stirring used during the shell fabrication, a kinetic controlled process is expected, rather than diffusional control. The crossing point (-0.23, -6.50) of the anodic and cathodic branches of these two reactions determines the displacement potential of -0.23 V vs SCE and the corresponding current density of $e^{-6.5}$ 0.0015 A/cm$^2$. Therefore, using an average particle diameter from the TEM micrographs of 3.2 nm, having an average surface area of $3.22 \times 10^{-13}$ cm$^2$, results in an average reaction rate of $2.51 \times 10^{-21}$ moles/s/particle.

In the absence of Cu(II) ions the Co nanoparticle is expected to be anodized by protons in the electrolyte, leading to the complete loss of the Co solid nanoparticle to Co(II) ions. The fact that Co nanoparticles are preserved in the aqueous acidic environment is another confirmation of the Cu shell formation.

Magnetoresistance (MR) of the pressed Co-Cu core-shell nanoparticle pellet was tested by the standard 4-probe method as described in Chapter 1. As shown in Figure 3.14 (a), the observed fluctuation of the MR as a function of field at 10 K indicated there is no presence of the induced antiferromagnetic behavior. Figure 3.14 (b) shows the positive temperature coefficient of the resistance, which is an indicator of the metallic conduction rather than the thermally activated behavior with a negative temperature coefficient.
Figure 3.14 (a) Magnetoresistance as a function of the applied magnetic field at 10 K, and (b) resistance as a function of temperature for the pressed Co-Cu core-shell nanoparticle pellet.
3.4 Summary

Co-Cu nanoparticles and microparticles were synthesized and characterized. Core-shell structure nanoparticles and microparticles were fabricated by a displacement reaction between the Co core and Cu(II) ions in an aqueous electrolyte. XANES results are consistent with the encapsulation of the Co nanoparticles by Cu without any significant cobalt oxide. The cobalt core in the nanoparticles retains the same fcc phase as the precursor cobalt nanoparticles, while mixed hcp and fcc phases were observed for the cobalt microparticles coated with a copper shell. The magnetization of the Co nanoparticle was retained when it was protected by the Cu shell and exposed to air. SQUID and XRD results verify again that the cobalt in core-shell particles is free from oxidative impurities. The copper shell around cobalt was also found to be responsible for the enhancement in magnetic properties, such as blocking temperature and magnetic moment. An estimate of the displacement rate of cobalt atoms with copper ions was calculated to be $2.51 \times 10^{-21}$ moles/s/particle. The pressed Co-Cu core-shell nanoparticle pellet follows the metallic conduction rather than the thermally activated behavior. There is no GMR observed in this system even though the metallic conduction is followed in the Co-Cu core-shell nanoparticles.

3.5 References


CHAPTER 4 COBALT-GOLD CORE-SHELL NANOPARTICLES

A gold shell was fabricated around the cobalt nanoparticles in an organic solvent (tetrahydrofuran). The resulting structure and magnetic behavior of the Co-Au core-shell nanoparticles are reported in this chapter. The use of an organic solution rather than an aqueous one was chosen due to the instability of the gold salt at low pH, causing precipitation. The low pH is required to avoid cobalt oxide formation. The advantage of a gold shell over a copper shell is the easy functionization of gold with organic molecules or macromolecules by thiol chemistry, and the added corrosion resistance imparted by a much nobler metal. In this chapter, the synthesis of the gold shell around the cobalt nanoparticle and the characterization is discussed in the first section, and then in section 2 the annealing effect on the Co-Au core-shell nanoparticle structure and magnetic properties are presented.

4.1 Synthesis and Characterization of Co-Au Core-Shell Nanoparticles

4.1.1 Experimental

- **Gold Shell Formation around Cobalt Core Nanoparticles**

  The cobalt nanoparticles, obtained by the method described in Chapter 2, were added to a 50 ml KAuCl$_4$ (0.024 M) in THF solution under untrasonication. In order to prevent the oxidation of the precursor cobalt nanoparticle during gold shell formation, the synthesis was carried out in a glove box. The initial brown colored solution changed to blue indicating that the gold ions oxidized the cobalt surface atoms on the cobalt nanoparticles. The reaction was continued for an additional 1 hour. The core-shell nanoparticles were washed thoroughly with THF and dried under nitrogen condition.
**Characterization**

The morphology of the Co-Au core-shell nanoparticles was investigated using transmission electron microscopy (TEM, JEOL 2010) with an accelerating voltage of 200 kV. The magnetic properties of the Co-Au core-shell nanoparticle were tested using a SQUID magnetometer (Quantum Design Inc., model MPMS 5S). Temperature dependent magnetization and field dependent magnetization were performed for the Co-Au core-shell nanoparticles, following the same procedures as described in Chapters 2-3.

The physicochemical interaction between the SB3-12 and Co-Au core-shell nanoparticle was investigated under transmission mode with FT-IR spectroscopy (Thermo Nicolet Nexus 670). The pure surfactants were ground with KBr and compressed into a pellet, their spectra were recorded as a reference spectrum to be compared with those of the Co-Au core-shell nanoparticle sample. The UV/vis sample was Co-Au core-shell nanoparticles suspended in ethanol. UV/vis spectra were recorded in a 1 cm width cuvette at room temperature using Genesys™ 10 spectrophotometer. X-ray diffraction (XRD) was carried out using the CPS120 Inel curved position sensitive detector system utilizing Co Kα radiation source, which is located in Lawrence Livermore National Laboratory. The powder samples for XRD were loaded into a sealed aluminum container with a kapton film window.

**4.1.2 Results and Discussion**

The easy oxidation of cobalt on the nanoparticle surface, occurring before shell formation or during the shell formation, will prohibit the gold shell uniformity leading to the partial coating of the cobalt core. Two cases were examined: one, where the cobalt
nanoparticles were partially oxidized before coating and the other, when the cobalt nanoparticle precursor were not oxidized.

Figure 4.1 shows UV-vis spectrum of Co-Au core-shell nanoparticles in an ethanol solution. The presence of an absorption peak at 585 nm is due to the gold plasmon resonance, indicative of the formation of an Au shell around cobalt. It was reported that the Co nanoparticles have no plasmon resonance peak in this UV region.\textsuperscript{1,2} A large red shift of the plasmon absorption when compared with pure gold nanoparticles (\textasciitilde 530 nm)\textsuperscript{3} could be attributed to the presence of a cobalt core and also indicated that almost no free gold nanoparticles were formed in the displacement reaction consistent with the literature report on gold coated silver nanoparticles.\textsuperscript{4,5} Such a shift was previously observed in the case of gold coated $\gamma$-Fe$_2$O$_3$ core-shell nanoparticles,\textsuperscript{6} gold coated silver nanoparticles\textsuperscript{4,5,7} and for a silver shell around a silica core.\textsuperscript{8}

\textbf{Figure 4.1} UV/vis spectrum of the Co-Au core-shell nanoparticle ethanol solution
Figure 4.2 shows representative bright-field TEM images of Co-Au core-shell nanoparticles. The nanoparticles were found to be nearly monodisperse with a size of 2.7 nm ± 0.5 nm (the size was calculated using Scion software from Scion Corporation for counting more than 150 nanoparticles). The image contrast, which is directly related to differences in the atomic number or projected specimen mass thickness, has been used as a distinguishing criterion for the core-shell structure.\textsuperscript{9-11} High resolution TEM image in the inset of Figure 4.2 shows the contrast between the cobalt core and the gold shell. It can be inferred from the HRTEM image that even though the thickness of the gold shell around the cobalt core was not uniform, it appeared to completely coat the cobalt core. Hollow interiors as reported in the case of silver core gold shell nanoparticles\textsuperscript{4} were not observed in these cobalt core gold shell nanoparticles, indicating a self-limiting reaction. This could be attributed to ultrasonic stirring, the use of THF as the solvent, and the smaller cobalt nanoparticle template. The ultrasonication was anticipated to favor a uniform reaction over the cobalt nanoparticle surface. The reaction rate in THF solution was anticipated to be slower, due to the weaker ionic strength in organic solution, as compared with the reaction rate in the aqueous solution, possibly preventing the local formation of gold particles around the cobalt surface. The smaller size of cobalt nanoparticle will favor the faster reaction over almost the entire surface rather than over a partial surface region around the cobalt nanoparticle due to the higher surface to the volume ratio in smaller particles. The formation of a more spherical shell rather than other shapes is due to its lower surface energy compared with other shapes due to the Ostwald ripening process.\textsuperscript{4,5} The gold shell thickness was also estimated based on the weight percentage of gold in the core-shell nanoparticles (Au wt%=38.1, determined from atomic absorption analysis) and the particle
size from TEM, assuming a bulk density. The thickness of the shell was calculated to be 0.67 nm, which is in agreement with the value obtained from the HRTEM image.

![TEM image of Co-Au core-shell NPs](image)

**Figure 4.2** TEM image of Co-Au core-shell NPs (inset shows the HRTEM of single particle)

The structure of the Co-Au core-shell nanoparticles was studied by X-ray diffraction (XRD) with a cobalt radiation source rather than copper radiation source to try to enhance the cobalt core signal. The pattern of the Co-Au core-shell nanoparticles is shown in Figure 4.3 and the peaks with lattice distance of 0.233, 0.204, 0.145, and 0.124 nm were assigned to the (111), (200), (220) and (311) reflection planes of fcc gold, respectively. The pattern only shows the gold diffraction signal without cobalt diffraction
signal. This is attributed to the outer gold shell, which blocks the X-ray diffraction from the cobalt core.

Figure 4.3 XRD spectra of Co-Au core-shell nanoparticle and oxidized Co nanoparticle

Figure 4.4 shows the Co K-edge XANES spectra of the hcp cobalt foil, Co-Au core-shell nanoparticles with and without oxidation, and two standard cobalt oxides as references. No oxidation was observed in the Co-Au core-shell nanoparticle synthesized under nitrogen protection as evidenced by the spectra similarity between the cobalt foil and the core-shell nanoparticle (Fig 4.4, Co-Au NPs A). For core-shell nanoparticles that are partially oxidized (Fig 4.4, Co-Au NPs B), the increase of the white-line and the absence of the inflection point indicated partial oxidation of the cobalt core. The oxidization was
also observed in a gold coated iron nanoparticle synthesized by the reverse micelle method conducted in an organic solution consistent with the XANES analysis.\textsuperscript {12}

\textbf{Figure 4.4} Co K-edge XANES spectra of a hcp cobalt foil, Co-Au nanoparticles (A, synthesized in glove box; B, synthesized with some oxidation), standard two cobalt oxides (CoO and Co\textsubscript{2}O\textsubscript{3}) as reference spectra

Figure 4.5(a) shows the magnetic property of the Co-Au core-shell nanoparticle with oxidation, compared to the Co nanoparticle data from Chapter 1. The blocking temperature, determined from the maximum of the zero-field cooled (ZFC) curve, indicates the transition from the superparamagnetic state to the ferromagnetic state. The maximum point was not observed within the range of the experiment and indicated that the blocking temperature is above room temperature, which is much higher than that of pure
cobalt nanoparticle with a blocking temperature of 124 K. The existence of the hysteresis loop, Figure 4.5 (b) (non-zero values of the coercivity and the remnant magnetization) at 300 K also confirms the ferromagnetic state of the Co-Au core-shell nanoparticles. The oxidation of the cobalt core is also indirectly observed by the shape of the hysteresis loop. The asymmetry of the hysteresis loop shown in Figure 4.5 (b) indicates that the magnetization of the Co-Au core-shell nanoparticles is dependent on the applied magnetic field. This asymmetric hysteresis loop also shows a two-step saturation behavior which is similar to the reported iron oxide coated iron nanoparticles.\textsuperscript{13} The rapidly saturated part corresponds to the ferromagnetic cobalt cores, while the slowly saturated part is attributed to the cobalt oxide.

![Figure 4.5](image)

**Figure 4.5** (a) ZFC and FC magnetization of cobalt nanoparticles and Co-Au core-shell nanoparticles with partial oxidation at an applied field of 100 Oe; (fig. continued)
Figure 4.5 (Continued) (b) magnetic hysteresis loop of fresh Co-Au nanoparticles at 300 K and 10 K (FC signifies that the sample was cooled from room temperature to 10 K with an applied field of 5 Tesla)

The field cooled hysteresis loop was measured by cooling the sample from 300 K to 10 K in an applied field of 5 Tesla, then resetting the field to zero before the data collection. FC hysteresis loop shift was observed in comparison with the ZFC hysteresis loop as shown in Figure 4.5(b), which indicates that partial cobalt core was oxidized. This is consistent with the XANES analysis as shown in Figure 4.4.

Figure 4.6 shows the magnetic results of the Co-Au core-shell nanoparticles without oxidation that were synthesized under nitrogen protection. The blocking temperature is above room temperature as indicated by the loss of the maximum in the
ZFC magnetization (inset, Figure 4.6) and the non-zero value of coercivity. Therefore, the gold shell influences the magnetic property. The lower FC slope in the M-T curve as shown in the inset of Figure 4.6 also indicated that the intraparticle interaction is strong and affects the magnetic property.

Figure 4.6 Field dependent magnetization at 300 K and 10 K (both ZFC and FC at 5 Tesla) for Co-Au core-shell NPs without oxidation; the right inset shows the enlarged partial M-H curve (x and y labels to the right insert are the same as the main graph) and the left inset shows the ZFC and FC temperature-dependent magnetization M-T curve at 100 G.

The physicochemical interaction between the SB3-12 and the nanoparticle was investigated by FT-IR. Figure 4.7 shows the FT-IR spectra of the pure SB3-12 and the
SB3-12 bounded to the Co-Au core-shell nanoparticles. The strong bands at 2919 cm\(^{-1}\) and 2851 cm\(^{-1}\) are assigned to the asymmetric and symmetric CH\(_2\) stretching modes, respectively, similar to for the cetyltrimethylammonium p-toluene sulfonate (CTAPS) stabilized copper nanoparticles and the SB3-12 stabilized cobalt nanoparticle as discussed in Chapter 2. It was reported that the shape (narrowness and the wavenumber location) of the FT-IR spectra was an indicator of the physicochemical interaction between the surfactant and the nanoparticles.\(^{14,15}\) For a pure surfactant, there are two broad bands in this region of 1540 – 1440 cm\(^{-1}\). The first peak at 1488 cm\(^{-1}\) is attributed to the asymmetric mode of the CH\(_3\)-(N\(^+\)) group, and the second at 1467 cm\(^{-1}\) is assigned to the CH\(_2\) scissoring mode,\(^{16,17}\) which is also similar to the peak assignments in the CTAPS stabilized copper nanoparticles.\(^{14}\) These two peaks shift to lower wavenumbers when the surfactant is coated on the nanoparticles, suggesting a less mobile environment and a strong association of these functional groups on the surface of the nanoparticles. The quaternary ammonium group coordinates to the surface of the nanoparticle and protects the nanoparticle from agglomeration.\(^{14}\) The symmetric stretching mode of the S-O is observed as a bimodal broad band around 1275 and 1150 cm\(^{-1}\). The narrowing of these peaks for the surfactant bounded to the nanoparticles indicates the relatively lower mobility of these functional groups in the coated Co-Au core-shell nanoparticle samples. FT-IR proves the existence of SB3-12 and chemically bound to the Co-Au core-shell nanoparticle surface even after the displacement reaction and the tetrahydrofuran washing process.

4.1.3. Summary

In this section, the synthesis of Co-Au core-shell nanoparticle in organic solution was discussed. The synthesized Co nanoparticle is easily oxidized, even with exposure to
trace air during the fabrication process. The gold shell has a dramatic effect on the magnetic properties. The blocking temperature is above room temperature at an applied magnetic field of 100 G. The SB3-12 surfactant is still bound to the nanoparticle surface after the gold coating and prevents the agglomeration of the nanoparticles.

Figure 4.7 FT-IR spectra of the SB3-12 and SB3-12 stabilized Co-Au core-shell NPs

4.2 Annealing Effect

A granular structure with a nanometric ferromagnetic layer separated by a non-magnetic layer is a homogenous mixture of nanometric, ferromagnetic phases in a non-magnetic matrix. The magnetization orientation of the discrete particles will align parallel
to each other by applying a magnetic field to overcome the antiferromagnetic coupling, thus reducing the spin-dependent scattering and the subsequent resistivity.

The factors effecting the extent of GMR include: size of the discrete phase, distance between the two magnetic layers (nonmagnetic layer thickness), composition of the granules, shape of the GMR materials, and the interface between the particles and the matrix. GMR performance of the thin film is also dependent on the post thermal treatment. Annealing can reduce the structural disorder, but also increase the particle size and interparticle distance as observed in the electrodeposited Co-Cu nanogranular alloyed thin films. The two different materials in magnetic and nonmagnetic layers need to be immiscible or they will lose the interface between the two phases by diffusion into each other. Kahn has reported the phase diagram of cobalt-gold and shown that the gold and cobalt are immiscible. In the cluster-based materials, it normally requires high field to overcome the anisotropy energy of the particles with various shapes and to align their magnetic moments.

In this section, the nonmagnetic-shell and magnetic-core nanoparticles have been used to create a novel granular material by pressing the particles together and heating. It is the first time, to the best of the author’s knowledge, that this type of nano-granular fabrication approach has been successfully demonstrated. The microstructures, magnetic properties, physicochemical interaction between the SB3-12 and the Co-Au core-shell nanoparticles, and magnetoresistance were studied for Co-Au core-shell nanoparticles after being annealed at different temperatures.
4.2.1 Experimental

In order to study the structure effect on the magnetic properties and GMR behavior, the prepared Co-Au core-shell nanoparticle was annealed at different temperatures: 200 °C, 250 °C, 450 °C and 600 °C under hydrogen gas flow in a quartz tube situated in a tubular furnace. The annealing temperature was increased to a desired temperature within 30 minutes and that temperature was maintained for 2 hours. The granular sample for the GMR measurement was prepared by a cold-press method. The applied pressure was 5000 Psi (Presser model: Carzer Hydraulic 3912) and the pressing duration time was 2 minutes.

The morphology of the annealed Co-Au core-shell nanoparticle was examined by transmission electron microscopy (TEM, JEOL 2010) with an accelerated voltage of 200 kV. Scanning electron microscopy (SEM, Cambridge S-260) was used to study the sample annealed at 600 °C due to the poor solubility in THF or ethanol.

The existence of the SB3-12 surfactant in the annealed Co-Au core-shell nanoparticle samples was investigated under transmission mode with the FT-IR spectroscopy (Thermo Nicolet Nexus 670). The pure surfactants were ground with KBr and compressed into a pellet, their spectra were recorded as reference spectra to be compared with those of the annealed Co-Au core-shell nanoparticle samples.

Magnetic properties and magnetic field dependent resistance were tested following the same procedures as described in Chapter 3.

4.2.2 Results and Discussion

Figure 4.8 (a-c) shows the TEM bright field micrographs of the annealed Co-Au core-shell nanoparticles at different temperatures and the corresponding selected area
electron diffractions in the insets. After annealing the Co-Au core-shell nanoparticles, the particle size increases with an increase of the annealing temperature. After 200 °C annealing, the particle has an average size of 6.7 nm with a standard deviation of 1.0 nm. The average particle size increases to 9.1 nm with a standard deviation of 2.6 nm for Co-Au core-shell nanoparticles annealed at 250 °C. With further increase of the annealing temperature, the average particle size increased to 13.0 nm with a standard deviation of 3.6 nm, and 53.3 nm with a standard deviation of 9.7 nm, for the Co-Au core-shell nanoparticle annealed at 450 °C and 600 °C, respectively. The particle size for the Co-Au core-shell nanoparticles at 600 °C was characterized by SEM due to the poor solubility of the nanoparticle in the solvent. For the Co-Au core-shell nanoparticles annealed at 200 °C, SAED rings, from inner to outer, correspond to the lattice spacing of 0.233, 0.201, 0.140, 0.121 and 0.112 nm, which are characteristic of gold. There was no carbon observation in this annealing process, indicating no decomposition of SB3-12 and consistent with the reported SB3-12 decomposition point (250~260 °C). For Co-Au core-shell nanoparticles annealed at 250 °C, the following rings 1, 2, 3, 4 and 5 were observed with plane spacing of 0.233, 0.201, 0.147, 0.123 and 0.108 nm, which are again characteristic of gold. The weak inner ring is due to the formation of carbon with a calculated lattice spacing of 0.317 nm corresponding to the (002) plane of carbon. The SAED patterns for Co-Au core-shell nanoparticles annealed at 450 °C are similar to those of the 250 °C annealed Co-Au core-shell nanoparticles. However, a significant difference is that the patterns in the 450 °C annealed sample are more spots than the 250 °C annealed sample, which reflects the more crystalline and larger size particles.
Figure 4.8 TEM bright field micrographs of Co-Au core-shell nanoparticles annealed at (a) 200 °C, (b) 250 °C, (fig. continued)
Figure 4.8 (continued) (c) 450 °C, respectively; and (d) SEM microstructure of the Co-Au core-shell nanoparticles annealed at 600 °C.

FT-IR was used to monitor the presence of the SB3-12 after the annealing process. Figure 4.9 shows the spectra of the pure SB3-12, and the annealed Co-Au core-shell
nanoparticles at different temperatures (200, 250, 450 and 600 °C). The spectrum of the SB3-12 bound on the Co-Au core-shell nanoparticles after being annealed at lower temperature (200 °C and 250 °C) exhibits the characteristic peaks of SB3-12. This indicates that the presence of the SB3-12 surfactant was observed even after 2 hours of annealing at 250 °C. The peaks disappeared after the annealing was completed at 450 °C and 600 °C, which indicates the complete decomposition of the surfactant.

Figure 4.9 FT-IR spectra of the SB3-12, SB3-12 stabilized Co-Au core-shell nanoparticles annealed at 200 °C, 250 °C, 450 °C and 600 °C.
Figure 4.10 (a-d) shows the magnetic property of the annealed Co-Au core-shell nanoparticles at different temperatures. The coercivity and remnant magnetization are the axes intersection points of the hysteresis plot in Figure 4.10. The nonzero values of the coercivity and the remnant magnetization for all the annealed samples indicate that the annealed nanoparticles are ferromagnetic, which is consistent with the temperature dependent magnetization as shown in the upper-left insets of Figure 4.10. The oxidation of the magnetic core in the core-shell structure was studied by the shift of the field cooled hysteresis loop as compared with the hysteresis loop without an applied filed. An obvious shift was observed in all the annealed samples, this indicates that the gold shell has not effectively protected the cobalt core from oxidation.

Figure 4.10 Field dependent magnetization at 300 K and 10 K (ZFC and FC at 5 Tesla) for Co-Au core-shell nanoparticles annealed at (a) 200 °C, (fig. continued)
Figure 4.10 (Continued) (b) 250 °C, (c) 450 °C and (d) 600 °C, respectively. The left inset shows the enlarged partial M-H curve and the right inset shows the ZFC and FC M-T curve. (fig. continued)
Figure 4.10 (Continued) (d) 600 °C, respectively. The left inset shows the enlarged partial M-H curve and the right inset shows the ZFC and FC M-T curve.

The coercivity increases and then decreases with a change in the annealing temperature as shown in Figure 4.11 (a). This trend is due to the increase of the particle size after the annealing process. As the particle size increases within the single domain with an increase of the annealing temperature, the coercivity increases. The coercivity decreases when the particle contains multiple magnetic domains. The change of the particle size was observed in Figure 4.8 (a-d) and the annealing effect behavior on the coercivity of Co$_{100-x}$Cu$_x$ granular alloys has also been reported.$^{25,26}$ The ratio of the remnant magnetization (Mr) to the saturation magnetization (Ms), or squareness, decreases with an increase of the annealing temperature as shown in Figure 4.11 (b). Both the coercivity and the Mr/Ms are higher at the lower measuring temperature.
Figure 4.11 (a) Coercivity as a function of the annealing temperature; and (b) ratio of the remanent to the saturation magnetization as a function of the annealing temperature.

Figure 4.12 (a) shows the magnetic-field dependent resistance for fresh Co-Au core-shell nanoparticles. A negative magnetoresistance was observed at 10 K. In the pellet of the Co-Au core-shell nanoparticles, the cobalt cores, serving as magnetic scattering centers, is random without an applied field resulting in a spin-disordered state. The magnetic moment of the cobalt cores will align to each other by applying a magnetic field, thus reducing the spin-dependent scattering and the subsequent resistance. This observation is similar to a recent reported of MR in gold coated iron nanoparticles fabricated by a sequential reverse micelle method, where an MR of only 0.23 % at 5 K was reported.\textsuperscript{27,28} Here, the value is larger, 0.35 % at 10 K. Similar to the Fe-Au core-shell nanoparticles study,\textsuperscript{27,28} the temperature-dependent resistance as shown in the inset of Figure 4.12 (a) shows a positive temperature coefficient of resistance, characteristic of metallic conduction. This observation indicates that the Co-Au core-shell nanoparticles are...
still metallic even with the existence of SB3-12 surfactant chemically bounding on the surface.

Figure 4.12 (b) shows the effect of the pressing time on the magnetic-field dependent resistance for Co-Au core-shell nanoparticles annealed at 250 °C. The almost overlapping MR curve indicates that the pressing time has little effect on the MR during the measured time duration.

**Figure 4.12** MR as a function of applied field at 10 K for (a) the Co-Au core-shell nanoparticles without annealing treatment (inset shows the temperature-dependent resistance at zero applied magnetic field); (fig. continued)
Figure 4.12 (continued) (b) the Co-Au core-shell nanoparticles annealed at 250 °C pressed for 2 minutes and 10 minutes.

Figure 4.13 (a) shows the magnetic-field dependent resistance for the Co-Au core-shell nanoparticles annealed at different temperatures. The inset of Figure 4.13 (a) shows temperature dependent resistance at zero magnetic field with a positive slope indicating that the Co-Au core-shell nanoparticles exhibit metallic conduction similar to the fresh Co-Au core-shell nanoparticle as shown in Figure 4.12 (a). The annealing effect has a dramatic effect on MR. There is a large increase in MR when the sample was annealed at 200 °C, then the MR decreases with an increase of the annealing temperature within the range of temperature study. This observation is consistent with the reported melt-spun Co-Cu granular alloys, where MR increased and then decreased with an increase of the annealing temperature.\textsuperscript{22,26,29,30} A maximum MR of about 1.5% was observed for the Co-Au core-
shell nanoparticle annealed at 200 °C. It was reported that the maximum MR value occurred for particle diameters around the electron mean free path.\textsuperscript{30,31}

Another factor that may play a role in the MR change is the difference in interparticle interaction (dipolar interaction) after annealing at different temperature. It was predicted that both the MR and the sensitivity of the MR to the external field are reduced with the introduction of the dipolar interaction.\textsuperscript{30} In the normalized FC curve, the magnetization decreased as the temperature increased for the Co-Au core-shell nanoparticles annealed at lower temperature (200 °C and 250 °C) and increased as the temperature increased for the Co-Au core-shell nanoparticles annealed at higher temperature (450 °C and 600 °C), which can be used to evaluate the particle interaction.\textsuperscript{32-35} The smaller slope in the normalized FC magnetization indicates a stronger interparticle interaction. The normalized FC magnetization curves (Figure 4.13 (b)) show differences in slopes. The lower the annealing temperature, the lower the slope. This indicates that the particle interaction increases with an increase of the annealing temperature. Thus, the decrease of the MR and the sensitivity to the external field is attributed to the increase of the dipolar interaction with the increase of the annealing temperature. The MR value does not reach its saturation even at higher applied magnetic field, which is consistent with the recent review reported granular nanomaterials.\textsuperscript{24}
Figure 4.13 (a) MR as a function of applied field at 10 K for the Co-Au core-shell nanoparticles annealed at 200 °C, 250 °C, 450 °C and 600 °C. (Inset shows the typical temperature-dependent resistance at zero applied magnetic field); (b) FC magnetization of the Co-Au core-shell nanoparticles annealed at different temperatures (normalized at 340 K).
4.2.3 Summary

FT-IR analysis showed that the SB3-12 was chemically bound with Co-Au core-shell nanoparticles even after the displacement reaction. The particle size increases with an increase of the annealing temperatures. SB3-12 was still chemically bound with the nanoparticles after lower-temperature annealing and decomposed after high-temperature annealing. The annealing process has a dramatic effect on magnetic properties. Coercivity increases and then decreases with an increase of the annealing temperature, while the ratio of the remanent to saturation magnetization decreases with an increase of the annealing temperature. Also, the magnetoresistacnc decreases with an increase of the annealing temperature. It is the first demonstration of CoAu nanoparticles exhibiting magnetoresistance.

4.3 References


J. Umemura, D. G. Cameron, and H. H. Mantsch, Biochimica et Biophysica Acta 602, 32-44 (1980).


CHAPTER 5 IRON NANOPARTICLES DISPLACEMENT WITH COPPER IONS

The methodology developed for the fabrication of Co-Cu core-shell particles in aqueous electrolyte as reported in Chapter 3 was extended to iron nanoparticles. However, the method was observed to be limited under the same conditions used for the Co-Cu system. There was no copper shell formation around the iron nanoparticle. The resulting nanoparticle was pure copper. The detailed results are reported in this chapter.

5.1 Experimental

- Synthesis of Iron Nanoparticles

The iron nanoparticles were synthesized following the procedure similar to those of the cobalt nanoparticles. A mixture of 3-(N,N-dimethyldodecylammonium)-propanesulfonate (SB3-12) (0.3523 g, 1.05 mmol) and 10 mL of superhydride (1 M lithium hydrotriethyl borate in tetrahydrofuran (THF) solvent) in 50 mL THF was added dropwise to a mixture of 0.5163 g (4.065 mmol) Fe(II)Cl₂ in 50 mL THF solution under ultrasonication and under nitrogen protection. The reaction was continued for an additional hour and was quenched by adding ethanol. The solution was left undisturbed and the iron nanoparticles precipitated by sedimentation. The iron nanoparticles were then washed thoroughly with THF and dried under vacuum condition.

- Displacement reaction

The procedure and solution for the Co-Cu core-shell nanoparticle fabrication were used for the reaction between the iron nanoparticles and the copper ions.

- Characterization
Nanoparticles were characterized by transmission electron microscopy (TEM) operated on a JEOL 2010 microscope with a 200 kV accelerating voltage, and UV/vis spectrophotometer, as discussed in Chapter 3.

The electrochemical reaction rates were characterized on a rotating disk electrode (RDE) using linear sweep voltammetry, (Solartron SI1287 and 1255B), as presented in Chapter 3. A copper disk working electrode was used to characterize the kinetic range of the copper reduction reaction, and an iron disk working electrode was used to characterize the anodization of iron. The counter electrode was copper during the copper reduction study and platinum during the iron anodization case.

5.2 Results and Discussion

![Figure 5.1 Pourbaix diagram of Fe system](image)

**Figure 5.1** Pourbaix diagram of Fe system\(^1\)
The Pourbaix diagram for the Fe system is shown in Figure 5.1. Similar to the Pourbaix diagram for the Co system, the equilibrium between Fe and Fe(OH)$_2$, the hydrated form of FeO, is not stable and will dissolve in solution with pH lower than 6. The FeO will exist in solution at a pH higher than 6. As mentioned in Chapter 3 for the reaction between the cobalt nanoparticle and the electrolyte solution, proton and copper ions will compete to react with the magnetic core. Here, the chosen pH is 4 for the iron nanoparticle case and was the same as the solution used with the cobalt nanoparticles.

TEM bright field micrographs of both the synthesized iron nanoparticles and the iron-displaced-copper nanoparticles are shown in Figure 5.2. The iron precursor nanoparticles shown in Figure 5.2 (a) have a mean size of 6.2 nm with a standard deviation of 1.3 nm. The selected area electron diffraction (SAED) pattern shown in the inset of Figure 5.2 (a) consists of bcc iron and iron oxides. Diffraction rings 1, 3 and 4 have a lattice distance of 0.255 nm, 0.167 nm and 0.151 nm arising from the reflections of the of (311), (511) and (440) planes, respectively, for iron oxides. The other 2 and 5 rings with a lattice distance of 0.203 nm and 0.143 nm arise from the (110) and (200) planes, respectively, for body-centered-cubic (bcc) iron. The undesirable iron oxide signature was possibly due to the sample transfer into the TEM. This observation indicated that the SB3-12 has effectively protected the iron nanoparticle from agglomeration but failed to prevent the iron nanoparticle from oxidation. The easy oxidation of iron nanoparticles was also reported in the thermal decomposition method$^{2,3}$ and sonochemical method.$^4$

TEM was carried out on the Fe particles after exposure to the Cu(II) solution. The observed spherical particle in Fig 5.2 (b) has an average size of 6.5 nm (standard deviation of 1.6 nm), which is comparable to the size of the synthesized iron nanoparticles (6.2 nm).
The corresponding EDS elemental analysis as shown in the inset of Figure 5.2 (c) shows only Cu, C, O and Au peaks without Fe peak. The C, O and Au signals are from the TEM grid. Thus, the elemental analysis proves that the iron nanoparticles after immersion into the Cu(II) solution became copper nanoparticles, and not a core-shell structure. In other words, the Cu(II) ions completely oxidized the Fe core to form a Cu nanoparticle.

The UV/vis spectra of the original iron nanoparticles and the resulting copper nanoparticles are shown in Figure 5.2 (c). No plasmon resonance peak was observed for the SB3-12 stabilized iron nanoparticles and the absorption decreases with the increase of the wavelength; while for the resulting Cu nanoparticles, a plasmon resonance peak at around 578 nm was observed. The observed red shift compared to pure copper nanoparticles (566 nm) here can be attributed to the size larger than 4 nm.\textsuperscript{5}

\textbf{Figure 5.2} TEM bright field micrograph of (a) the SB3-12 stabilized Fe nanoparticles (inset shows the selected area electron diffraction pattern), (b) Cu nanoparticles synthesized by the displacement reaction; (fig. continued)
Figure 5.2 (Continued) and (c) UV/vis spectra of SB3-12 stabilized iron THF solution and aqueous copper nanoparticle solution (inset shows the EDAX micro mapping of the nanoparticles after the displacement between the Fe and Cu)

The displacement reaction rate was estimated from the kinetic regime in the Fe-Cu Evans diagram, shown in Figure 5.3. The crossing point (-0.26, 6.14) of the anodic and cathodic branches of these two reactions determines the displacement potential of -0.26 V vs SCE and the corresponding displacement current density of \( (e^{-6.14}) = 0.0022 \text{ A/cm}^2 \). The sudden drop of the current density at high voltage for the iron is due to the passivation of the surface from the formation of iron oxides.
Since a similar copper displacement current density was observed with cobalt and iron nanoparticles (0.0022 and 0.0015 A/cm²), a difference in reaction rate cannot be responsible for the fact that a Cu shell forms with the Co nanoparticle and not the Fe nanoparticle. The crystalline structure then may be a possible factor in whether a shell forms or not. The Co nanoparticles are of the fcc structure (Figure 2.2) while the Fe nanoparticles are bcc (Figure 5.2 (a)). Atoms in a fcc or/and hcp structure can pack together closer than they can in the bcc structure. The packing factor (the volume of atoms in a cell per total volume of a cell) is 0.74 for fcc and hcp crystals. However, the packing factor in a bcc unit cell is only 0.68. The mismatch between the crystalline units (lattice constant) and the lower packing factor in the bcc structure may favor a more porous shell leading to the continual reaction of the copper ions into the Fe core eventually destroying
the whole iron nanoparticles. A mathematical description of the displacement reaction will be presented in Chapter 8.

5.3 Summary

Spherical copper nanoparticles were obtained from the iron nanoparticles due to complete displacement of the iron core. The observation is in direct contrast to the displacement reaction with cobalt that resulted in a Co-core and Cu-shell. The difference between the displacement reaction of the Cu(II) ions with Fe and Co was attributed to the difference in the Fe and Co structure.

5.4 References

1 M. Pourbaix, Altas of Electrochemical Equilibria in Aqueous Solutions (Cebelcor, Houston, Texas, U.S.A).


6.1 Introduction

Soft magnetic materials with a suitably high saturation magnetization (about 20 kilogauss) are required for the development of advanced electromagnetic devices. Iron-cobalt alloys are of interest for high temperature soft magnets due to their high Curie temperature, and high magnetization. The FeCo alloyed nanoparticles with high saturation magnetization are promising candidates for in vitro biological cell separations due to the magnetophoretic mobility of the magnetic compounds. However, the control of the Fe and Co composition in nanoparticles fabricated by various techniques is not straightforward, as it does not always reflect the amount of Fe and Co as reactants. For example, it was observed that starting with equal atomic amounts of Fe$^{2+}$ and Co$^{2+}$, in a sol-gel process with a SiO$_2$ matrix, the composition of the synthesized FeCo nanoparticle was not an equimolar solid phase of FeCo. It was also reported that the aerogel method is better in controlling composition due to the easy reduction in the aerogel samples compared to the xerogel method. The difference between the aerogel and xerogel method is that the former can easily fabricate the FeCo alloy nanoparticle with a desired composition without the formation of a mixture of unalloyed cobalt, metal oxide and FeCo alloy nanoparticle.

In this Chapter, the synthesis of the FeCo alloyed nanoparticles was discussed and the characterized results presented. The annealing effect of the FeCo structure and magnetic properties were investigated. In addition, the displacement of the FeCo nanoparticle with copper ions was evaluated.
6.2 FeCo Nanoparticle Fabrication

- Synthesis

The SB3-12-stabilized FeCo alloyed nanoparticles were synthesized similar to our reported cobalt nanoparticles, in Chapter 2. Briefly, the procedure is: (1) addition of 0.135 g (1 mmol) cobalt (II) chloride and 0.138 g (1 mol) iron (II) chloride to 50 ml THF solvent in the two two-neck flasks, respectively; (2) Ultrasonic stirring to complete dissolution; and (3) mixing of the milky colored FeCl$_2$ solution and blue colored CoCl$_2$ solution with a blue solution. The volume was adjusted to 100 ml with THF. A mixture of 50 ml SB3-12 (0.505 g, 1.5 mmol) in THF and 30 ml of a superhydride-THF solution was added dropwise to the above mixed salt solution within half hour in a nitrogen protection environment. After adding the reducing agent into the blue THF solution containing iron (II) chloride and cobalt (II) chloride, the solution immediately turned black indicating the formation of the colloid nanoparticles. The untrasonication was continued for an additional 1 hour and the reaction was quenched by adding ethanol. The solution was left undisturbed overnight and the nanoparticles precipitated by sedimentation. The nanoparticles were then washed thoroughly with THF and dried under vacuum. The annealing temperature was 250 ºC and 450 ºC.

- Characterization

The morphology of the nanoparticles was characterized by transmission electron microscopy (TEM) (JEOL 2010) with an accelerating voltage of 200 kV and the samples were prepared by dropping THF solution of nanoparticles on an amorphous holey carbon coated copper grid. The interaction between the nanoparticle and the surfactant was tested under transmission mode by Thermo Nicolet Nexus 670 Fourier-transfer infrared (FT-IR)
spectrometer. The surfactants were ground with KBr and compressed into a pellet, their
spectra were recorded as a reference spectrum to be compared with those of the fresh and
annealed FeCo alloyed nanoparticle spectra.

Fe K-edge and Co K-edge XANES spectra were collected at the DCM beamline at
the 1.3 GeV electron storage ring of the Center for Advanced Microstructures and Devices
(CAMD) synchrotron radiation facility at Louisiana State University. The experiments
were performed in standard transmission mode using ionization chambers filled with
nitrogen at 1 atm pressure. The monochromator was equipped with Ge (220) crystals, and
the photon energy was calibrated relative to the absorption spectra of standard cobalt and
iron foils setting the first inflection point to 7709 eV for the cobalt foil spectrum and to
7112 eV for the Fe spectrum. Standard XANES data analysis was performed using the
WINXAS97 software package, where raw spectra were normalized and background
corrected by fitting the pre-edge region with a straight line, and the post-edge region with a
third order polynomial. Magnetic studies were carried out in the same way as described in
Chapter 3.

- Results and Discussion

Figure 6.1 shows the TEM bright field micrograph of the SB3-12 stabilized colloid
FeCo alloyed nanoparticles. The dark regions are nanoparticles. The SB3-12 stabilized
FeCo alloyed nanoparticles are well-dispersed with the size of 3.8 nm ± 0.3 nm. The clear
fringes shown in Figure 6.1 have an interplanar distance of 0.200 nm. After comparing the
fringe distance with the reported values for FeCo, Fe, and FeO, the measured d-spacing
corresponds to the (110) plane with the reported standard d-spacing of 0.202 nm of FeCo
(1:1 molar ratio) alloy. Since Fe and FeCo have a similar lattice constant and crystalline
structure, this observed d-spacing also could be the (110) plane with the reported standard d-spacing of 0.202 nm of Fe. The selected area electron diffraction (SAED) pattern as shown in the inset of Figure 6.1 shows the rings arising from the small size of the particle. Since the FeCo alloy has similar patterns as the iron in XRD and electron diffraction, the X-ray absorption spectroscopy was used to investigate the alloyed structure.

![TEM bright field micrograph of SB3-12 stabilized FeCo NPs (inset shows the selected area electron diffraction)](image)

**Figure 6.1** TEM bright field micrograph of SB3-12 stabilized FeCo NPs (inset shows the selected area electron diffraction)

The physicochemical interaction between the FeCo alloyed nanoparticles and the surfactant was investigated by FT-IR. The FT-IR spectra of the SB3-12 surfactant and the
freshly prepared SB12-stabilized FeCo nanoparticles are shown in Figure 6.2. Similar to the SB3-12 stabilized Co nanoparticle as discussed in Chapter 2 and the SB3-12 stabilized Co-Au core-shell nanoparticles as discussed in Chapter 4, the SB3-12 was found to be chemically bound to the nanoparticle surface, preventing the agglomeration of the nanoparticles.

![Figure 6.2 FT-IR spectra of the pure SB3-12 and SB3-12 bound on the FeCo nanoparticles.](image)

**Figure 6.2** FT-IR spectra of the pure SB3-12 and SB3-12 bound on the FeCo nanoparticles.

Figure 6.3 shows the magnetic property of the synthesized FeCo alloyed nanoparticles in powder form. Temperature dependent magnetization behavior as shown in the right inset of Figure 6.3 shows that the blocking temperature is well above room
temperature. As compared to the synthesized cobalt nanoparticles, the blocking temperature increased after the addition of the iron element. It was also higher than the Co-Cu core-shell nanoparticle and comparable to the Co-Au core-shell nanoparticles. The larger slope of the FC M-T curve (inset of Figure 6.3) indicated that the interparticle interaction plays a role in the higher blocking temperature here. The hysteresis loop at 300 K shows non-zero coercivity (5 Oe), which is consistent with the high blocking temperature. Larger coercivity (430 Oe) was observed at 10 K. The oxidation of the FeCo nanoparticles was examined by observing the shift of the field-cooled (5 Tesla) hysteresis loop in comparison with the zero-field-cooled hysteresis loop at 10 K. If the ferromagnetic metallic nanoparticles are oxidized, the hysteresis loop will shift toward the applied magnetic field direction due to the exchange-coupling between the ferromagnetic core and the antiferromagnetic oxide shell.\textsuperscript{10-13} The almost overlapping ZFC and FC hysteresis loop as shown in the inset of Figure 6.3 indicates that the amount of oxidation in the FeCo nanoparticles is negligible. This is expected since the nanoparticles were fabricated under nitrogen protection. It was also observed that the magnetization of FeCo nanoparticles did not saturate even at high field, which is different from the thin film or bulk FeCo alloyed materials. The saturation magnetization was determined from the intercept of the M vs $H^{-1}$ at high field.\textsuperscript{14} After consideration of the iron and cobalt content as determined by atomic absorption analysis in the SB3-12 stabilized nanoparticles, the saturation magnetization was calculated to be 19.2 KG. Assuming an average density of 7.794 g/cm$^3$, the saturation magnetization can also be expressed as 196.2 emu/g, where 1 emu/g = $4\pi\rho$ gauss. The saturation magnetization is lower in comparison with the bulk iron (220 emu/g) and higher than the bulk cobalt (162 emu/g). Higher saturation magnetization was observed here
compared to FeCo alloyed thin films as prepared by an alternative electrodeposition method. The observed saturation magnetization is much higher than that reported for 6 nm iron nanoparticles synthesized by thermal decomposition of iron pentacarbonal (82 emu/g).\textsuperscript{15}

![Hysteresis loop of fresh FeCo nanoparticles](image)

**Figure 6.3** Hysteresis loop of fresh FeCo nanoparticles (left-upper inset shows the temperature dependent magnetization at 100 G; right-bottom inset shows the enlargement of the hysteresis loop)

The oxidation state of the elemental iron and cobalt was investigated by the corresponding XANES spectra. Figure 6.4 (a) shows the Fe K-edge XANES spectra of a standard Fe foil, FeCo nanoparticles and the iron oxide as a reference; Figure 6. 4 (b) shows Co K-edge XANES spectra of the standard Co foil, FeCo nanoparticles and the
cobalt oxide as a reference. Both the position of the absorption edge and the white line intensity are similar to those of the corresponding standard foils as shown Figure 4 (a) and (b). The chemical shift of the absorption edge to higher energies, lower pre-edge intensity and a higher white line evident in the spectra of the stand cobalt oxide and iron oxide were not observed in the FeCo nanoparticles, indicating that the nanoparticles are not oxidized and the oxides are present in trivial amount.

Figure 6.4 (a) Fe K-edge XANES spectra of standard Fe foil, FeCo nanoparticles and the iron oxide as a reference; (fig. continued)
The phase structure of the FeCo nanoparticles was analyzed by comparing their spectra to those of the standard bcc iron and hcp cobalt foils. XANES analysis was utilized for the FeCo alloyed nanoparticle in alumina matrix and silica matrix.\textsuperscript{6-8} Figure 6.5 compare the XANES spectra at the Fe and Co edge of the same FeCo nanoparticle sample after shifting the Co K-edge data to the Fe K-edge energy for convenience. The standard bcc iron and cobalt foils have distinctly different fingerprints arising from the local coordination geometry of the absorbing atoms. The Fe K-edge XANES spectrum and the energy-corrected Co K-edge XANES spectrum have the same oscillations as the standard
iron foil rather than the cobalt foil. Although there are some deviations from the reference iron spectrum in the region of the absorption edge and the first series of strong shape resonances located between about 7150 and 7175 eV, the positions of the shape resonances at higher excitation energies are in good agreement with those of the iron foil. Since pure cobalt nanoparticles have an fcc phase and iron nanoparticles have a bcc phase, the observed bcc phase indicated that the cobalt atoms are alloyed with iron atoms to form the bcc structure. The reduction in the intensity is due to the surface effects and the increased local disorder in the nanoparticle sample as compared with the standard foil. Thus, the existence of the bcc alloyed FeCo nanoparticle was confirmed by the local geometry (absorbing atom) study on both the iron and cobalt atoms in the FeCo nanoparticles.

![Figure 6.5](image.png)

**Figure 6.5** K-edge XANES spectra of the cobalt foil, iron foil, FeCo nanoparticles. (Cobalt K data was shifted to iron K-edge energy in order for comparison).
6.3 Annealing Effect

The effect of the annealing environment on the FeCo nanoparticles was investigated by using nitrogen and hydrogen at 250 °C. Figure 6.6 (a) and Figure 6.7 (a) show the TEM micrograph of the annealed nanoparticle in nitrogen and hydrogen environment, respectively. In both situations, spherical nanoparticles and cubic nanoparticles were observed. Figure 6.6 (b) and Figure 6.7 (b) show the selected area electron diffraction (SAED). The obvious inner ring was arising from the carbon, which is due to the decomposition of SB3-12 at higher temperature. High resolution HRTEM image (Figure 6.6 (c) and Figure 6.7 (c)) shows a nanocube with a clear lattice fringe indicating the nanocrystalline structure. The uniform network structure of the lattice fringe in the nanocube shows a defect-free structure. A careful study of the lattice fringes with an interplanar distance of 0.44 nm corresponding to (105) plane of Fe₂O₃ indicated that the nanocube in Figure 6.6 (c) is iron oxides (Fe₂O₃) rather than the alloyed FeCo nanoparticles. The observed iron oxide rather than the homogeneous FeCo alloyed nanocube indicates that sintering occurred during the annealing process and a trace of oxygen either from the surfactant or air leakage leading the oxidation of the segregated irons. Figure 6.6 (d) shows electron microdiffraction for the nanocube in Figure 6.6 (c). The diffraction spots were generated from the surface of one nanocube. Figure 6.7 (d) shows the SAED of the Figure 6.7 (c). The electron microdiffraction for the cube-rich area shows the spot without order, which is due to the different orientation of the nanocube surface. The FeCo alloyed nanoparticles were also observed in the annealed nanoparticles as seen in Figure 6.7 (e). The clear fringes have an interplanar distance of 0.20 nm similar to Figure 6.1. The measured d-spacing corresponds to (110) plane with a reported d-
spacing of 0.202 nm of FeCo alloy. As previously mentioned, Fe and FeCo have similar lattice constants and crystalline structure, therefore, the observed d-spacing could also be the (110) plane with reported d-spacing of 0.202 nm of Fe. The larger nanocubes in the nitrogen annealed sample suggests that more nanoparticles sintered and grew together before carbon formation occurred, preventing the formation of the larger size nanocube.

**Figure 6.6** TEM bright field micrographs of FeCo NPs annealed at 250 °C under nitrogen atmosphere (inset shows the selected area electron diffraction) (fig. continued)
Figure 6.6 (Continued) TEM bright field micrographs of FeCo NPs annealed at 250 °C under nitrogen atmosphere

Similar to FeCo nanoparticles annealed under nitrogen, the FeCo nanoparticles annealed at 250 °C shows the Fe$_2$O$_3$ nanocube as seen in Figure 6.7 (e) and FeCo metallic nanoparticle as seen in Figure 6.7 (f). The Fe$_2$O$_3$ shows a square shape and the FeCo shows a spherical shape. This indicated that the annealing process lead to the segregation of the
FeCo nanoparticle and the more reactive Fe will react with the trace oxygen present during transfer or from the oxygen element of the surfactant during its decomposition process.

Figure 6.7 TEM bright field micrographs of FeCo NPs annealed at 250 °C under hydrogen atmosphere (inset shows the selected area electron diffraction). (fig. continued)
Figure 6.7 (Continued) (e) and (f) are the enlarged square and the sphere in Figure (c).

Figure 6.8 and Figure 6.9 show the magnetic behavior of the FeCo alloyed nanoparticles annealed at 250 °C in nitrogen and hydrogen environments, respectively. ZFC and FC temperature study (right-upper inset of the Figure 6.8 and 6.9) shows the blocking temperature is well above room temperature. It was observed that the applied magnetic field at 1 Tesla and 0.01 Tesla has a dramatic effect on the magnetic behavior of the nanoparticle sample during the ZFC and FC temperature-dependent magnetization measurement as seen from the right-upper inset in Figure 6.8. The increased magnetization and the appearance of the peaks in the ZFC at higher field indicate that the blocking temperature is a field dependent parameter. The small shift of the coercivity at 10 K between ZFC and FC (5 Tesla) hysteresis loops in the nitrogen annealed sample (the left-bottom inset of Figure 6.8) indicates partial oxidation of the nanoparticle, which is consistent with the above TEM analysis. The overlapping of the coercivity as shown in
Figure 6.9 indicates that nanoparticles under hydrogen annealing have less oxide than the nanoparticle annealed under the nitrogen condition. In addition, the saturation magnetization is much higher in the hydrogen annealed sample than the sample annealed in nitrogen environment. This observation is attributed to the larger amount of the cubic shape nanoparticle in the hydrogen annealed sample, the different interfacial effect, and the more oxides in the nitrogen annealed sample which would decrease the saturation magnetization dramatically. Here, the annealing environmental plays a role in the oxide formation. As compared with nitrogen, hydrogen is a reducing agent which favors the pure metallic nanoparticle. Hydrogen can thus reduce the oxides that form from “trace” oxygen in the gas or during transfer, which couldn’t happen in the nitrogen environment.

Figure 6.8 Hysteresis loop of FeCo NPs annealed at 250 °C under nitrogen condition (left-upper inset shows the temperature dependent magnetization; right-bottom inset shows the enlargement of the hysteresis loop)
The effect of the annealing temperature on the FeCo alloyed nanoparticle was investigated by choosing temperature at 450 °C in the hydrogen environment. The morphology and the selected area electron diffraction of the annealed samples are shown in Figure 6.10 (a) and (b), respectively. Annealed nanoparticles with different shapes such as sphere, pearl, core-shell and cube were observed with a broad size distribution. The inner ring of the SAED shows the existence of the carbon. A clear shell was observed in the annealed nanoparticles as shown in Figure 6.10 (a). Figure 6.10 (c) and (d) shows the HRTEM image of nanocube and the nanocube-rich microdiffraction, respectively. The clear lattice fringe in Figure 6.10 (c) shows the nanocube is defect free. After careful examination of the fringe distance with 0.20 nm, this nanocube cannot be iron oxide, thus
it is either elemental Fe or FeCo alloy. The edges of the nanocube are not straight, which arises from the balance between the formed carbon shell as template to limit the informality (straight edge or spherical shape) and the pushing force from minimizing the surface energy effect with a spherical shape. The complete decomposition of the surfactant as evidenced by FT-IR spectra (shown in Figure 6.11) suggests that there is a carbon shell after the 450 °C annealing process.

**Figure 6.10** TEM bright field micrographs of FeCo NPs annealed at 450 °C under hydrogen atmosphere (inset shows the selected area electron diffraction); (fig. continued)
Figure 6.10 (Continued) Figure (e) is enlarged part of the Figure (c).

Figure 6.11 FT-IR spectra of the pure SB3-12, SB3-12 bound to the nanoparticle and the annealed samples, respectively.

Figure 6.12 shows the magnetic behavior of the FeCo nanoparticles annealed at 450 °C in hydrogen environment. The ZFC curve (the right-upper inset of Figure 6.12)
shows the large particles possess blocking temperature well above room temperature. The inflection points at 36 K and 148 K indicate that there is a certain amount of smaller size nanoparticles after annealing consistent with the TEM observation. The lower saturation magnetization as compared with the fresh SB3-12 stabilized FeCo nanoparticle and 250 °C annealed nanoparticle sample is due to the existence of a large amount of small size nanoparticles as observed by TEM and the existence of the large amount of iron oxides, which was evident by a shift of the FC hysteresis loop as comparison with ZFC hysteresis loop (right inset of Figure 6.12).

![Hysteresis Loop](image)

**Figure 6.12** Hysteresis loop of FeCo NPs annealed at 450 °C under hydrogen condition (left-upper inset shows the temperature dependent magnetization at 100 G; right-bottom inset shows the enlargement of the hysteresis loop)

A further oxidation study was carried out with XANES. The shift of the pre-edge position, reduced intensity of the pre-edge peak and a higher white line were observed for the annealed samples in comparison with the Fe and Co foil as shown in Figure 6.13 (a) and (b). This indicated some oxides were present in the annealed nanoparticle sample.
These differences are significantly more pronounced in the Fe K-edge spectra indicating a higher degree of oxidation for iron atoms. Co K-edge spectra show much less oxidation probably due to the oxygen atoms bonding preferentially to iron arising from the more active iron than the cobalt. For both elements, more oxides were observed for the sample annealed at 450 °C than the sample annealed at 250 °C. This is consistent with the observed decreased saturation magnetization with the increase of the annealing temperature.

Figure 6.13 (a) Fe K-edge XANES spectra of standard Fe foil, annealed FeCo nanoparticle samples, and the iron oxide as a reference; (fig. continued)
Figure 6.13 (Continued) (b) Co K-edge XANES spectra of the standard Co foil, annealed FeCo nanoparticle samples, and the cobalt oxide as a reference.

The existence of FeCo alloyed nanoparticles was further proven by the comparison of the XANES resonance. Figure 6.14 shows the K-edge spectra of the Fe and the shifted Co-edge of the iron and cobalt foils and the annealed nanoparticles. It was observed that even after annealing, the spectra are still similar to the bcc foil spectrum rather than the cobalt foil indicating the existence of the bcc FeCo alloyed structure. The most visible deviations appeared in the Fe K-edge spectrum after annealing at 450 °C can be explained by additional structures appearing at the energy positions of the shape resonances of the iron oxides. Also, the intensity of the spectra at higher energies increases with the increase of annealing temperature, indicating larger and better ordered structures.
Figure 6.14  K-edge XANES spectra of the cobalt foil, iron foil, FeCo nanoparticles annealed at 250 °C and 450 °C. (Cobalt K data was shifted to iron K-edge energy in order for comparison).

6.4 Displacement of FeCo Nanoparticles with Copper Ions

Displacement reaction between the SB3-12 stabilized FeCo nanoparticles and the copper ions was also studied. TEM bright field image of the nanoparticles is shown in Figure 6.15. The particle has an average size of 3.75 nm with a standard deviation of 0.72 nm. The size is comparable to the precursor FeCo nanoparticles. Elemental composition of the nanoparticles was carried out by atomic absorption analysis (AAA). The weight percentage is 0.51 %, 0.65% and 97.6% for Fe, Co and Cu, respectively. Similar to the Co-
Cu core-shell nanoparticle assumption, the calculated core size is about 0.87 nm and the shell is about 2.88 nm.

Figure 6.15 TEM images of the FeCo-Cu nanoparticles

The magnetic study shows the synthesized nanoparticles were superparamagnetic at room temperature and has a blocking temperature of 126 K as shown in Figure 6.16. It is lower than that of the Co-Cu and Co-Au core-shell nanoparticles. This is due to the smaller magnetic core than those in the Co-Cu or Co-Au core-shell nanoparticles. The blocking temperature is strongly dependent on the magnetic nanoparticle size. The displacement reaction occurred to a greater extent than either the Co-Cu or Au-Cu core-shell nanoparticles, but the core was not completely destroyed as in the Fe case.
The saturation magnetization was determined by the intercept of magnetization vs $H^{-1}$ at high field. After considering the Fe and Co weight percentage the calculated saturation magnetization based on cobalt and iron is 35.4 emu/g and 93.1 emu/g at 10 K and 290 K, respectively. The obtained saturation magnetization is much lower than the fresh FeCo precursor nanoparticles. This is due to the smaller size of the FeCo nanoparticles after the displacement reaction.

![Hysteresis loop of the FeCo nanoparticle after displaced with copper ions. (The inset shows the zero field cooled temperature-dependent magnetization measured at a field of 100 G)](image)

**Figure 6.16** Hysteresis loop of the FeCo nanoparticle after displaced with copper ions. (The inset shows the zero field cooled temperature-dependent magnetization measured at a field of 100 G)

### 6.5. Summary

The SB3-12 stabilized colloidal FeCo alloyed nanoparticles were synthesized by a facile wet chemical reduction method with SB3-12. The annealing temperature and the
annealing medium have a dramatic effect on the shape and the magnetic properties. The oxidation and the segregation of the Fe and Co phase were observed in the annealed FeCo nanoparticles. A small amount of Fe and Co was observed after the displacement between the FeCo nanoparticles and copper ions, which resulted in diminished magnetic properties.

6.6 References


CHAPTER 7 METALLIC CORE NANOPARTICLES WITH NON-METALLIC SHELLS

7.1 PMMA Stabilized Zero Valence Metallic Nanoparticles

7.1.1 Introduction

Iron nanoparticles have applications in magnetic data storage,\(^1\) possibly as a catalyst for the fabrication of carbon nanotubes/nanofibres,\(^2\) and in biomedical systems such as improving the quality of magnetic resonance imaging (MRI) and site-specific drug delivery.\(^3-5\) However, one challenge related to the application of iron nanoparticles is the prevention of the facile oxidation that occurs in ambient environments and acidic solutions. One conventional method to avoid iron nanoparticle oxidation is to coat the nanoparticle with a more noble metal or ceramic shell. An alternative shell material is poly(methyl methacrylate) (PMMA), of interest because of a variety of applications noted in Chapter 1 (i.e. form robust film to affix implants and remodel lost bone).

Here, we report a facile room-temperature wet chemical reduction method to synthesize PMMA stabilized colloidal metallic nanoparticles reduced from chloride salts by lithium hydrotriethyl borate (superhydride). There is no need for additional surfactant or stabilizer. To the best of the author’s knowledge, this is the first demonstration of the synthesis of PMMA stabilized zero-valent metallic nanoparticle by an in-situ chemical reduction method. However, in-situ magnetic polymeric nanocomposite preparation by a high-temperature thermal or high-intensity ultra-sonochemical decomposition method has been reported.\(^6-10\) Compared with the high-temperature thermal or high-intensity ultra-sonochemical decomposition methods, the method adopted here is more economical, and easy to carry out at room temperature. The obtained colloidal nanoparticles can be easily
solidified into PMMA nanocomposite thin films during a solvent vacuum evaporation process under ultrasonic stirring at room temperature. The zero-valent state of iron nanoparticles was investigated by X-ray absorption near-edge structure (XANES) analysis and magnetic analysis. The effect of iron loading in the nanocomposite on the magnetic properties was investigated by changing the starting PMMA concentration. This method can be applied to other metal nanoparticle synthesis systems and an example of gold nanoparticle synthesis was provided with its morphological characterization and optical property test. Due to the ferromagnetic property at room temperature, the synthesized Fe-PMMA nanoparticles have potential wide applications in the information storage media, magnetic refrigeration, audio reproduction, ferrofluids, magnetically guided drug delivery.

7.1.2 Experimental

- **Materials**

  Iron (II) chloride (FeCl$_2$, anhydrous, beads, 99.99%, packaged under argon), potassium tetrachloroaurate (III) (KAuCl$_4$, 99.9%, anhydrous beads), and tetrahydrofuran (THF, 99.90% pure packaged under nitrogen), lithium triethyl borohydride (superhydride) as 1 M solution in THF, and ethanol (reagent anhydrous, water < 0.003%) were purchased from Aldrich chemical company. Standard poly(methyl methacrylate) (PMMA, Mw=80,000) was purchased from Goodfellow Company. All the chemicals were used as received without further treatment.

- **Synthesis of the PMMA stabilized zero-valence metallic nanoparticles**

  The reducing agent (20 ml superhydride in 50 ml tetrahydrofuran) was added to the mixture of FeCl$_2$, and PMMA in THF (50 ml) solution (7.1 mM FeCl$_2$, 5% PMMA) drop by drop within half hour and reacted for 1 additional hour. The PMMA stabilized iron
nanoparticles were precipitated by adding ethanol, the supernatant solution was removed and the remaining black paste was re-dissolved again in THF and re-precipitated using ethanol. The above process was repeated three times in order to remove LiCl and possible by-products such as BEt$_3$ (triethyl boron). The black paste that was obtained was dried under vacuum and dissolved in THF to form a stable colloidal solution. The effect of iron nanoparticle loading on the magnetic properties was conducted by changing the starting PMMA weight concentrations: 1% PMMA stabilized gold nanoparticles were synthesized following the same procedure as above.

- **Characterization**

Transmission electron microscopy (TEM) measurements were performed on a JEOL 2010 microscopy. Transmission electron microscope (TEM) samples were prepared by dissolving the obtained dried PMMA stabilized nanoparticles into tetrahydrofuran (THF) solvent under ultrasonic stirring condition, then deposited on an amorphous carbon coated Cu grid and dried in nitrogen protection condition. The Fe weight percentage in the iron nanoparticle complex was analyzed by atomic absorption spectroscopy elemental analysis. Fourier transform infrared spectroscopy (FT-IR) was used to test the possible physicochemical interaction between PMMA and iron nanoparticles, and the effect of the superhydride on the PMMA functional group. FT-IR spectra were recorded in the Thermo Nicolet Nexus 670 FT-IR spectroscopy with transmission mode after background reduction. The PMMA dispersant was compressed into a pellet; the spectrum was recorded as a reference spectrum to be compared with that of the PMMA stabilized nanoparticles. The UV-vis spectra of the THF colloidal gold nanoparticle solution with different
concentrations were recorded in a 1 cm width cuvette at room temperature using a Genesys™ 10 spectrophotometer.

Fe K-edge XANES spectra were collected at the Double-Crystal Monochromator (DCM) beamline at the 1.3 GeV electron energy storage ring synchrotron radiation facility of the Center for Advanced Microstructures & Devices (CAMD) at Louisiana State University, with the same procedure as outlined in Chapter 6.

The magnetization studies were carried out using a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer. The procedure was the same as described in Chapters 2, 3, 4, and 6.

7.1.3 Results and Discussion

Ultrasonic stirring was reported⁶ to play a vital role in the carbonyl salt thermal decomposition and subsequent metal nanoparticle formation. Here, no color change was observed before adding the reducing agent indicating that ultrasonic stirring has no effect on the reduction of the Fe(II) chloride salt. This is due to the increased stability of the chloride salt compared to the carbonyl salt used in the literature.

Figure 7.1 shows a typical bright field TEM micrograph of the PMMA stabilized iron nanoparticles on a holey carbon coated copper grid. Fe nanoparticles with a mean size of 5 nm (standard deviation of 0.6 nm) were observed. Considering no diffraction from PMMA due to its amorphous state, the observed dense electron diffraction ring patterns rather than spot diffraction patterns, shown in the inset of Figure 7.1, were due to the small size of the nanoparticles. The diffraction rings (from inside to outside) with a lattice distance of 0.243 nm, 0.204 nm, 0.143 nm, 0.104 nm, are assigned to the (111) line of
cubic iron oxide (FeO), and the (110), (200) and (220) of the bcc metallic iron structure. The partial oxidation of iron was due to the transfer of the sample to the TEM machine. The clear lattice fringe in the TEM bright field image indicates the highly crystalline structure of the iron nanoparticles (nanocrystals).

Figure 7.1 TEM bright field micrograph of PMMA stabilized iron nanoparticles (inset shows the selected area electron diffraction).
Due to the low concentration of iron nanoparticles in the Fe-PMMA nanoparticle complex, X-ray diffraction didn’t show any observable crystalline peaks. Therefore, XANES was used to investigate the valence state of iron nanoparticles. Figure 7.2 shows the Fe K-edge XANES spectra of PMMA stabilized iron nanoparticles, prepared under nitrogen, bcc iron foil, and iron oxides as references. Based on such factors as the position of the absorption edge, the intensities of the pre-edge and white line features, and other resonances, the nanoparticle spectrum is very similar to that of the bcc foil and different from any of the iron oxides. This observation indicates that the synthesized iron nanoparticles have bcc structure without oxidation. It also indicates that the iron nanoparticles are stable in the ethanol solvent during the washing process, unlike iron oxidation in the gold coated iron nanoparticles obtained from the microemulsion technique.\textsuperscript{11}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{xanes_spectra}
\caption{XANES spectra of the bcc iron foil, PMMA stabilized iron nanoparticles and iron oxides.}
\end{figure}
Figure 7.3 FT-IR spectra of pure PMMA and PMMA stabilized iron nanoparticles with PMMA concentration of 5% and 1% (wt)

It was reported that the superhydride is a strong reducing agent and can reduce esters, amides and other potentially desirable ligand functional groups.\textsuperscript{12,13} As an ester group, (\(\text{O}\))\(\text{C}=\text{O}\)) PMMA was anticipated to be reduced by the superhydride. The effect of the superhydride on the PMMA, and the possible physicochemical interaction between the iron nanoparticles and the PMMA were tested by FT-IR. The spectra of the PMMA and the synthesized PMMA stabilized powder nanoparticles are shown in Figure 7.3. The sharp absorption at 1732 cm\(^{-1}\) corresponds to C=O groups;\textsuperscript{14,15} the peaks at 1149 and 1192 cm\(^{-1}\) are due to the C-H deformations, and 1242 and 1269 cm\(^{-1}\) represent C-C-O stretch coupled with C-O stretch in PMMA.\textsuperscript{14} The similarity of the spectra between the PMMA and the PMMA stabilized nanoparticle indicates that the superhydride had an insignificant effect
on the PMMA, and the iron nanoparticles were effectively stabilized by PMMA. In other words, the PMMA was not reduced by the superhydride. The shift of the peaks toward lower wavenumbers was an indicator of the chemical bonding of surfactant onto the nanoparticle surface.\textsuperscript{16,17} There is almost no change in the peaks (wavenumbers) between the pure PMMA and the 5% PMMA stabilized Fe nanoparticles, indicating that the interaction between the iron nanoparticle core and the PMMA is through a weak physical force rather than a strong chemical bonding force; a similar spectra was also observed in the PMMA stabilized gold nanoparticle synthesized by the ex-situ polymerization of methyl methacrylate monomer in the presence of gold nanoparticles.\textsuperscript{15} This observation indicates that most of the PMMA is either physically bound to the nanoparticle or exists without contact with nanoparticles. However, diluting the PMMA concentration (from 5\% to 1\%) in the Fe-PMMA nanoparticle system, resulted in a strong shift of the C=O group from 1732 cm\textsuperscript{-1} to 1706 cm\textsuperscript{-1}, indicating that PMMA was bound to the Fe nanoparticle through the C=O functional group. The new peak around 3407 cm\textsuperscript{-1} was undoubtedly due to the O-H stretch,\textsuperscript{18} which is an indicator that part of the PMMA has decomposed into a carboxylic acid group during the synthesis or washing process. The formation of the acidic functional group can be explained by the hydrolysis of PMMA in the presence of the ethanol or traces of water during the synthesis or washing process, which was proposed recently for the formation of PMMA stabilized metal oxide nanoparticles.\textsuperscript{19,20} This suggests that PMMA forms a micelle cage around the iron nanoparticles by physical adsorption.\textsuperscript{21} The repulsive electrostatic force and steric interaction among the cages prevent the iron nanoparticle from agglomeration arising from attractive particle-particle forces such as van der Waals and magnetic forces.\textsuperscript{21} In addition, the higher viscosity of the
PMMA solution as compared with other surfactant solutions, and the reduction in the particle surface tension with the wrapping of PMMA layers\textsuperscript{21} are other important factors that lead to the discretely dispersed nanoparticles.

Figure 7.4 shows the hysteresis loop of the dried PMMA-Fe nanoparticles in the film form. Saturation magnetization (Ms) was determined by the intercept of magnetization vs $H^{-1}$ at high field.\textsuperscript{22,23} The calculated saturation magnetization was 84.8 emu/g based on the pure iron nanoparticles (elemental iron percentage in the Fe-PMMA nanoparticle complex was 7.59 wt % determined by atomic absorption elemental analysis). This saturation magnetization is lower than that of the bulk iron (220 emu/g). However, it is consistent with the reported magnetization value (25 to 190 emu/g for the size around 6 nm to 20 nm) for vapor deposited iron nanoparticles, and with that of iron nanoparticles (6 nm) synthesized by the thermal decomposition of iron pentacarbonal (82 emu/g).\textsuperscript{9,24} The decreased saturation magnetization was due to the particle size and the coating.\textsuperscript{9,24-27} The ratio of remanent magnetization (Mr) to saturation magnetization (Ms) was 0.13 at 300 K and 0.36 at 0 K, and the coercivity (Hc) was 106 Oe at 300 K and 1117 Oe at 10 K, shown in the left inset of Figure 4. These values indicate that the blocking temperature is above room temperature, \textit{i.e.} ferromagnetic at room temperature, which is different from the sonochemical synthesized poly (ethylene glycol) stabilized iron nanoparticles\textsuperscript{10} exhibiting a superparamagnetic property. Zero field cooled (ZFC) and field cooled (FC) temperature dependent magnetization measured at a constant field of 100 G was also provided in the right inset of Figure 7.4. The absence of the maximum peak in the ZFC temperature dependent magnetization curve indicates the ferromagnetic property of the PMMA
stabilized iron nanoparticles even at temperature of 340 K, which is consistent with the field dependent hysteresis loop results.

Figure 7.4 Hysteresis loops of PMMA stabilized Fe nanoparticles at 300 K, and 10 K at zero field cooled and field cooled at 5 Tesla (ZFC and FC hysteresis loops are almost overlapping at 10 K); the left inset shows the enlargement of the hysteresis loop and the right inset shows the ZFC and FC temperature dependent magnetization normalized by magnetization at 340 K measuring at a constant field of 100 G.

Magnetic measurements were also utilized to indirectly investigate the valence state of the iron nanoparticles. Zero-field cooled (ZFC) hysteresis loop at 10 K was compared to the field cooled (FC) hysteresis loop. The shift toward the applied magnetic field due to the exchange coupling interaction between the antiferromagnetic shell (FeO) and the ferromagnetic core (Fe)\textsuperscript{22,28-31} has been used as a criteria to distinguish the oxidation of the magnetic metal nanoparticles. The observed magnetization was almost overlapping (within the SQUID magnetometer measurement error) of the ZFC hysteresis.
loop and the FC (5 Tesla) hysteresis loop, \textit{i.e.} identical coercivities, Ms values and Mr/Ms ratios in both ZFC and FC conditions, indicates that the iron nanoparticles are free from oxidation, which is consistent with the XANES analysis and recent report on poly (ethylene glycol) stabilized iron nanoparticles.\textsuperscript{10}

The PMMA stabilized nanoparticles are ferromagnetic even at room temperature rather than the superparamagnetic characteristic of the bare iron nanoparticles. Considering that the observed nanoparticle is in the range of the single domain size, the intraparticle interaction plays an important role in the magnetic properties such as blocking temperature, coercivity and remanent magnetization. The high concentration of magnetic nanoparticles in the PMMA matrix increases the interparticle interaction and is responsible for the increased blocking temperature. The increased interparticle interaction pushes the Fe-PMMA nanocomposites into behaving like a continuous ferromagnetic thin film rather than the bare single domain iron nanoparticles, which was also observed recently in the high density of two-dimensional self-assemblies of cobalt nanoparticles.\textsuperscript{32}

The effect of iron nanoparticle loading was studied by changing the initial PMMA concentration in the reactant solution. Here, 1 wt. \% was used rather than the 5 wt. \%. The iron nanoparticle concentration was about 54.9 wt. \% as determined by atomic absorption analysis. Figure 7.5 shows the TEM bright field micrographs and Figure 7.6 shows the magnetic properties, respectively. It was observed that the PMMA concentration has a dramatic effect on the size of the iron nanoparticles. At lower PMMA concentration, the size can reach about 22 nm. The electron diffraction spot rather than the ring pattern indicates the bigger particle size consistent with TEM observation. The almost overlapping ZFC and FC hysteresis loops indicate that there is no obvious oxidation of the PMMA
stabilized iron nanoparticles. As determined from Figure 7.6, the coercivity was 58 Oe at 300 K and 161 Oe at 10 K, respectively. The saturation magnetization (based on the iron elemental percentage) was 184.4 emu/g at 300 K and 187.4 emu/g at 10 K, respectively. The coercivity decreased and the saturation magnetization increased as compared with the higher PMMA concentration. This is attributed to the increase of the iron nanoparticle size and the stronger intraparticle interaction arising from the low PMMA concentration.

Figure 7.5 TEM bright field image of Fe nanoparticle with low concentration PMMA (1 wt. %)
Figure 7.6 Hysteresis loops of PMMA stabilized Fe nanoparticles at 300 K, and 10 K at zero field cooled and field cooled at 5 Tesla (ZFC and FC hysteresis loops are almost overlapping at 10 K); the left inset shows an enlargement of the hysteresis loop and the right inset shows the ZFC and FC temperature dependent magnetization normalized by magnetization at 340 K measuring at a constant field of 100 G.

As proof of the generality of this method, PMMA stabilized gold nanoparticles were synthesized and the results are presented here. Figure 7.7 shows the transmission electron bright field micrograph of the synthesized PMMA stabilized gold nanoparticles dispersed on a amorphous holey carbon coated copper grid. The obtained nanoparticles have a spherical shape with a size around 9 nm. The left inset of the high resolution image and the right inset of the selected area electron diffraction patterns in Figure 7.7 indicate that the obtained gold nanoparticles are crystalline, similar to the PMMA stabilized iron
nanoparticles. The lattice fringes in the high resolution images showing a three-pedal spherical shape indicate that the growth of the gold nanoparticles are not along one specific crystalline plane in one direction, which was also noticed in electrodeposited Au-Fe, Au-Ni and Au-Co alloyed nanoparticles.\textsuperscript{33}

![Figure 7.7 TEM bright field micrograph of PMMA stabilized gold nanoparticles](image)

**Figure 7.7** TEM bright field micrograph of PMMA stabilized gold nanoparticles

Figure 7.8 (a) shows the UV-vis optical absorbance spectra of the PMMA stabilized tetrahydrofuran colloidal gold nanoparticles with different concentrations. A broad peak around 521 nm is related to the surface plasmon resonance absorption of gold nanoparticles, which arises from the interband transitions between the highly polarizable
Au 5d\textsuperscript{10} band and the unoccupied states of the conduction band.\textsuperscript{34} The existence of the plasmon resonance peak indicates the formation of the pure metallic gold nanoparticles.\textsuperscript{35-39} Figure 7.8 (b) shows the graph of the absorbance as a function of the gold nanoparticle concentration. The best fit line y=0.1029x+0.4443 with R\textsuperscript{2} value of 0.9885 is consistent with Beer’s law expected linear behavior of the absorbance with solute concentration for dilute solutions. The estimated absorption coefficient from the Beer’s law was 972 M\textsuperscript{-1}. cm\textsuperscript{-1} for wavelength at 521 nm.

**Figure 7.8** (a) UV/vis spectra of PMMA stabilized colloidal gold nanoparticle at 10 mM, 6 mM, 4 mM and 2 mM, respectively. (b) the absorbance dependence on the gold atoms concentration.

### 7.1.4 Summary

*In-situ* synthesis of PMMA stabilized colloidal nanoparticles were reported and the nanoparticles are well dispersed in THF solvent. It is the first demonstration of direct reduction of PMMA around an Fe core. PMMA has effectively prevented the iron nanoparticles from agglomeration. PMMA-iron nanoparticles were ferromagnetic even at room temperature. The concentration of PMMA has a dramatic effect on the synthesized nanoparticles, both in the size and the subsequent magnetic property. The PMMA
stabilized redox synthesized iron nanoparticle method combined with ultrasonic stirring
described here is a simple and general approach for the synthesis of zero-valence metallic
nanoparticles.

7.2 Carbon-coated Iron Nanoparticles

As discussed in Chapter 1, a carbon shell around magnetic nanoparticles has been
fabricated with potential applications in magnetic data storage. In this section, the
synthesis and characterization of 3-(N,N-Dimethyllaurylammonio)propanesulfonate, SB3-
12, stabilized iron nanoparticles and carbon-coated iron nanoparticles are presented. The
carbon shell was formed by directly annealing the surfactant bounded on the surface of the
iron nanoparticle. As compared with the reported methods as discussed in Chapter 1, the
fabrication of the carbon shell from the stabilized surfactant upon annealing is a simple and
cost effective alternative. To the best of the author’s knowledge, this is the first
demonstration of the formation of a carbon shell around iron nanoparticles by the direct
decomposition of the surfactant in the colloidal system.

7.2.1 Experimental

- Synthesis

The SB3-12 stabilized iron nanoparticles were synthesized similar to our previous reported
cobalt nanoparticles.40 A mixture of SB3-12 (0.3523 g), 10 mL superhydride (1 M lithium
hydrotriethyl borate in tetrahydrofuran) and 50 mL tetrahydrofuran was added dropwise to
the mixture of 0.5163 g Fe(II)Cl₂ in 50 mL tetrahydrofuran solution within half hour under
ultrasonication. The reaction was continued for an additional hour and then quenched by
adding ethanol. Iron nanoparticles were precipitated by sedimentation, and then washed
thoroughly with tetrahydrofuran and dried under vacuum condition. The annealing process was carried out under hydrogen gas flow in a quartz tube situated in a tubular furnace. The annealing temperature was increased to a desired temperature within 30 minutes and that temperature was maintained for 2 hours. The annealing temperatures used were 250 °C, and 450 °C. The stability of the carbon coated iron nanoparticles were tested by immersing the nanoparticles with untrasonication for over 20 hours in a sulfuric acid solution with a pH value of 1.5.

- Characterization

TEM, magnetic and FT-IR studies followed the same procedures as discussed in Chapter 2.

7.2.2 Results and Discussion

![Figure 7.9](image-url) TEM micrograph of SB3-12-stabilized iron nanoparticles
Figure 7.9 shows the TEM bright field micrograph of the SB3-12 stabilized colloidal iron nanoparticles. The dark areas are the iron nanoparticles and the lighter regions are the surfactant. The fresh iron nanoparticles with the size of 6.2 nm ± 1.3 nm are well-dispersed and self-assembled into 2-dimensional structures.

The FT-IR spectra of the SB3-12 surfactant and the freshly prepared SB3-12 stabilized iron nanoparticles are shown in Figure 7.10. The spectrum of the surfactant on the surface of the nanoparticles is similar to that of the pure surfactant. The strong bands at 2919 cm\(^{-1}\) and 2851 cm\(^{-1}\) are assigned to the asymmetric and symmetric CH\(_2\) stretching modes, respectively, similar to Salker et al.\(^{17}\) for the cetyltrimethylammonium p-toluene sulfobetaine (CTAPS) stabilized copper nanoparticles.\(^{17}\) It was reported that the shape (narrowness and the wavenumber location) of the FT-IR spectra was an indicator of the physicochemical interaction between the surfactant and the nanoparticles.\(^{16,17}\) The observed narrowing of the peaks in the surfactant bounded iron nanoparticles is attributed to the immobilization of the surfactant molecules on the particle surfaces.\(^{16,17}\) For pure surfactant, there are two broad bands in this region of 1540 – 1440 cm\(^{-1}\). The first at 1488 cm\(^{-1}\) is attributed to the asymmetric mode of the CH\(_3\)-(N\(^+\)) group, and the second at 1468 cm\(^{-1}\) is assigned to the CH\(_2\) scissoring mode,\(^{41,42}\) which is also similar to the peak assignments in the CTAPS stabilized copper nanoparticles.\(^{17}\) These two peaks overlap into one peak and shift to lower wavenumbers when the surfactant is coated on the iron nanoparticles, suggesting a less mobile environment, and a strong association of these functional groups on the surface of the iron nanoparticle. The quaternary ammonium group coordinates to the surface of the iron nanoparticle and protects the iron nanoparticle from agglomeration.\(^{17}\) The symmetric stretching mode of the S-O is observed as a bimodal
broad band around 1275 and 1150 cm\(^{-1}\). The narrowing of these peaks for the surfactant bounded to the iron nanoparticles indicates the relatively lower mobility of these functional groups in the coated iron nanoparticle samples. This observation is similar to the SB3-12 stabilized cobalt (Chapter 2), FeCo (Chapter 6) and Co-Au core-shell nanoparticles (Chapter 4).

Figure 7.10 FT-IR spectra of the SB3-12 and SB3-12-stabilized colloid iron nanoparticles.

Figure 7.11 shows the magnetic property of the synthesized SB3-12 stabilized iron nanoparticles in the powder form prepared under nitrogen protection. There is no hysteresis behavior observed at 300 K, as indicated by zero-values of coercivity and remanent magnetization, indicating the superparamagnetic state of the nanoparticles as is
expected. The superparamagnetic property at room temperature is consistent with the observation of iron nanoparticles having a size less than 9 nm at room temperature. A large coercivity (1320 Oe) was observed at 10 K. The oxidation of the iron nanoparticles was evident by observing a shift of the field-cooled (5 Tesla) hysteresis loop in comparison with the zero-field-cooled hysteresis loop at 10 K. Oxidized iron nanoparticles will shift the hysteresis loop toward the applied magnetic field direction due to the exchange-coupling between the ferromagnetic core and the antiferromagnetic oxide shell. The large difference between ZFC coercivity (1320 Oe) and FC coercivity (1586 Oe), as shown in the inset of Figure 7.11, indicates that the iron nanoparticles were partially oxidized in the sample preparation. The SB3-12 effectively prevented the iron nanoparticles from agglomeration, but did not prohibit the oxidation of the iron nanoparticles when exposed to trace oxygen.

**Figure 7.11** Field dependent magnetization of fresh Fe nanoparticles at 300 K and 10 K (both ZFC and FC at 5 Tesla); the inset shows the enlarged partial M-H curve.
Figure 7.12 (a) and (b) show the TEM bright field micrographs of the carbon coated iron nanoparticles after annealing under hydrogen condition for 2 hours at 250 °C and 450 °C, respectively. The carbon shell and the iron core can be easily discerned based on the contrast difference arising from the difference in the atomic numbers between the elements carbon and iron. The nanoparticle core size was about the same for the two cases (14.1 nm ± 3.6 nm). The carbon shell was thicker at the low annealing temperature (3 nm) compared to that at the higher annealing temperature (1.8 nm). The increase of the iron core after the annealing process may arise from the easy migration of the smaller particles and resulting sintering of other particles, which has also been observed in the annealing of cobalt or iron nanoparticles during the fabrication of a carbon shell by the carbon arc method,\textsuperscript{43,44} and in carbon nanotube formation by the CVD method.\textsuperscript{45} The use of hydrogen favors the reduction of any possible iron oxides formed during the nanoparticle synthesis.

\textbf{Figure 7.12} TEM micrograph of SB3-12 stabilized iron nanoparticles (a) annealed at 250 °C, and (b) annealed at 450 °C.
FT-IR was used to monitor the presence of the SB3-12 after the annealing process. Figure 7.13 shows the spectra of freshly prepared iron nanoparticles, and the annealed samples at different temperatures (250 °C and 450 °C). The presence of the SB3-12 surfactant was observed even after 2 hour annealing at 250 °C, while the peaks disappeared when annealing was done at 450 °C, indicating the complete decomposition of the surfactant. This observation is consistent with the reported SB3-12 melting point (250-260 °C).

![FT-IR spectra](image)

**Figure 7.13** FT-IR spectra of the fresh iron nanoparticles coated with SB3-12, and annealed iron nanoparticles at 250 °C and 450 °C, respectively.
Figure 7.14 Field dependent magnetization at 300 K and 10 K (both ZFC and FC at 5 Tesla) for iron nanoparticles annealed at (a) 250 °C; and (b) 450 °C; the inset shows the enlarged partial M-H curve.
The magnetic properties of the annealed samples shown in Figure 7.14 (a) and (b) are for iron nanoparticles annealed at 250 and 450 °C, respectively. Non-zero coercivity (291 Oe at 300 K and 575 Oe at 10 K for iron nanoparticles annealed at 250 °C; 254 Oe at 300 K and 663 Oe at 10 K for iron nanoparticles annealed at 450 °C) indicates that the carbon coated iron nanoparticles are ferromagnetic even at room temperature. The coercivity values at 10 K of the annealed samples are smaller than the freshly prepared uncoated iron nanoparticles (Fig 11), which reflects the lower coercivity of larger size nanoparticles. Similarly, the observed coercivity value here is higher than the reported value for the carbon coated iron nanoparticle fabricated by thermal segregation, having a 3 nm carbon shell thickness and 35 nm iron core, as expected since the iron core nanoparticles in this study are smaller. However, the coercivity is lower compared to a report carbon coated iron nanoparticles prepared by the arc method (56 nm core and much thinner shell around 3-4 graphitic layers), indicating an affect of the shell thickness.

Figure 7.15 shows the XRD patterns for the SB3-12-stabilized iron nanoparticles and annealed iron nanoparticles at the two different temperatures 250 °C and 450 °C. The observed peaks are characteristic of the nanoscale materials. The fresh nanoparticles show a bcc structure with a characteristic peak of (110). The annealed iron nanoparticle samples show the bcc iron peaks of (110), (200) and (211) and the graphite peak (004). The other peaks in the sample annealed at 450 °C are from the carbon signal. The XRD analysis indicates that there is no phase transition in the iron nanoparticles and no iron carbide formation after the annealing process. The weak carbon signal for iron nanoparticles annealed at 250 °C as compared with that of the iron nanoparticles annealed at 450 °C
indicates that most of the carbon formed at 250 °C is amorphous and most of the carbon is graphitic at 450 °C.

Figure 7.15 XRD pattern (1) iron nanoparticles, (2) and (3) iron nanoparticles annealed at 250 °C and 450 °C, respectively.

The effectiveness of the carbon shell in protecting the iron core from dissolution was tested by washing with pH=1.5 aqueous sulfuric acid solution. It was observed that the carbon-coated iron nanoparticles annealed at 250 °C generated hydrogen gas bubbles due to the oxidation/reduction reaction between the iron and the proton. A loss of the magnetic property was evident by a lack of particles attracted by a permanent magnet. Therefore, the acid treatment destroyed the 250 °C annealed iron nanoparticle and no further magnetic characterization was carried out. However, the iron nanoparticles annealed at 450 °C remained attracted to a permanent magnet after a 20 hr treatment with sulfuric acid without any observed hydrogen bubble formation. Thus, the carbon shell formed after the 250 °C
annealing process is porous, but is non-porous or ‘tight’ after the 450 °C annealing process, consistent with the FT-IR and XRD results, indicating a fully decomposed SB3-12 with a crystalline carbon shell.

A TEM bright field micrograph of carbon coated nanoparticles formed at 450 °C with acidic treatment for 20 hr is shown in Figure 7.16. The carbon shell and iron core are readily discerned, and the iron core size is 14.6 nm ± 5.4 nm, similar to in Figure 12 (b).

![Figure 7.16](image)

**Figure 7.16** TEM micrograph of carbon coated iron nanoparticles annealed at 450 °C after treatment with pH=1.5 sulfuric acid for 20 hrs.
The magnetic property of the acidic treated nanoparticles was also examined. Figure 7.17 shows the field dependent magnetization. The annealed nanoparticles retain the ferromagnetic property at room temperature, and there is no shift toward the applying field (ZFC and FC curve have the same coercivity) indicating that there is no oxide formation even after for 20 hour acidic treatment in ambient condition. This indicates that the carbon shell has effectively protected the iron nanoparticles from dissolution. At room temperature the coercivity was 338 Oe and at 10 K it was 721 Oe, slightly higher than the untreated annealed samples at 450 °C. As compared with the untreated carbon coated iron nanoparticles, the observed higher saturation magnetization after the acid treatment is believed to be due to the removal of the smaller carbon coated iron nanoparticles consistent with TEM observation.

![Field dependent magnetization](image)

**Figure 7.17** Field dependent magnetization at 300 K and 10 K (both ZFC and FC at 5 Tesla) for iron nanoparticles annealed at 450 °C with sulfuric acid treatment; the inset shows the enlarged partial M-H curve.
7.2.3 Summary

Non-porous carbon shells were fabricated around iron nanoparticles with a SB3-12 surfactant by annealing at 450 °C under hydrogen. The carbon shell protected the iron nanoparticles from dissolution while retaining the ferromagnetic property. Upon annealing, the size of the iron nanoparticles increased, and the room temperature magnetic property of the nanoparticles changed from superparamagnetic to ferromagnetic. Acid treated nanoparticles annealed at 450 °C retained the saturation magnetization and coercivity. At room temperature, the coercivity increased from zero to 254 Oe after annealing at 450 °C and was 338 Oe after acidic treatment. Acidic treated nanoparticles annealed at 250 °C showed that there is a loss of the ferromagnetic characteristic and, in addition, only partial decomposition of the surfactant and primary amorphous carbon formation are observed. After annealing at 450 °C, the ferromagnetic properties were retained, the surfactant completely decomposed, and a graphitic carbon structure resulted.

7.3 References


J. Umemura, D. G. Cameron, and H. H. Mantsch, Biochimica et Biophysica Acta 602, 32-44 (1980).


CHAPTER 8 CONCLUSIONS, MODEL SUMMARY AND FUTURE WORK

8.1 Conclusions

The sulfobetaine stabilized fcc crystalline cobalt (3.1 nm±0.5nm), bcc crystalline iron (6.2 nm±1.3 nm) and FeCo alloy (3.8 nm±0.3nm) nanoparticles were fabricated by the wet chemical reduction method and characterized. Magnetic studies show that the cobalt and iron nanoparticles are superparamagnetic at room temperature and ferromagnetic at 10 K, and that FeCo alloy nanoparticles are ferromagnetic. Sulfobetaine was found to be chemically bound to the nanoparticle surface and effectively protected the nanoparticles from agglomeration, but not against oxidation. Therefore, a shell around the nanoparticle was explored.

The displacement reaction between the copper aqueous electrolyte and the nanoparticles (Fe, Co and FeCo) was studied. A core-shell structure was observed in the Co-Cu (3.2 nm ± 0.6 nm) and FeCo-Cu (3.75 nm ± 0.72 nm) nanoparticles. This is the first demonstration of this technique in generating Cu shells around nanoparticles. There was no Fe-Cu core-shell nanoparticle formation; the iron nanoparticle was completely sacrificed by the copper ions with the formation of copper nanoparticles (3.75 nm ± 0.72 nm). Similarly, Co-Au core-shell nanoparticles (2.7 nm ± 0.5 nm) were fabricated by displacement, but in an organic solution. Sulfobetaine was still chemically bound to the Co-Au core-shell nanoparticle even after the displacement reaction and subsequent washing process.

Iron nanoparticles (5.0 nm ± 0.6 nm) as cores were coated with a poly(methyl methacrylate) (PMMA), which effectively protected the core from agglomeration and oxidation during the synthesis process. As compared with conventional methods, the
reported method here is easier to fabricate, economical, and the synthesized nanoparticles possessed ferromagnetic behavior at room temperature without observed oxidation, upon fabrication. The PMMA concentration in the reactant solution affected the product size and the subsequent magnetic property. The coercivity decreased and the saturation magnetization increased with the increase of PMMA concentration (from 1 wt. % to 5 wt. %). Furthermore, a tight carbon shell around iron nanoparticles (14.1 nm ± 3.6 nm) was formed directly by thermal decomposition of the bound surfactant, SB3-12. The carbon shell prevented the iron nanoparticle from oxidation in acid and retained its magnetic property. This is the first demonstration of the carbon shell formation by direct decomposition of the bound surfactant.

The shells around the cobalt-containing cores are different in thickness with 0.82 nm, 0.67 nm and 2.88 nm for the Co-Cu, Co-Au and FeCo-Cu core-shell nanoparticles, respectively. The shell thickness variation is due to the fact that the displacement reaction in not controllable. The thin metal shells surrounding the cobalt nanoparticle enables the cobalt core to be stable in air for a longer time and enhances the magnetic properties by increase the blocking temperature. However, the FeCo alloy nanoparticle (0.87 nm) coated with a thick copper shell had a decreased blocking temperature and lower saturation magnetization. The blocking temperature for the metallic shell cobalt core nanoparticle follows: Co (124 K) < FeCo-Cu (126 K) < Co-Cu (235 K) < Co-Au (above room temperature). The magnetic moment at room temperature follows: Co (0.70 \( \mu_B \)) < Co-Cu (1.63 \( \mu_B \)) < Co-Au (9.18 \( \mu_B \)). No coercivity was present in the fresh Co nanoparticles and Co-Cu nanoparticles at 300 K, while a large coercivity (1500 Oe) was observed in the Co-Au core-shell nanoparticles at room temperature. At 10 K the coercivity follows the
following order: Co-Au (1500 Oe) > Fe (1320 Oe) > Fe-PMMA (1117 Oe) > Fe-C (575 Oe) > Co (347 Oe) > Co-Cu (297 Oe) > FeCo-Cu (24 Oe).

The stability of the nanoparticle was assessed by exposure to air and was found to be in the order: Co-Cu > Co-Au > Co. The carbon shell coated iron nanoparticle was evaluated by exposure to acid and the results showed that this core-shell structure enabled the iron nanoparticle to remain stable, better than the Co-Cu system from the point of view of assessing the ferromagnetic property at room temperature.

After annealing, fcc cobalt nanoparticles transferred into an hcp crystal structure. The magnetic moment increased with an increase of the annealing temperature arising from the increased particle size, greater crystallinity and phase change. A similar increase in the particle size was observed for FeCo alloy nanoparticles. Phase segregation of FeCo occurred with the formation of iron oxide after annealing process, which results in the decrease of the saturation magnetization. The formation of cubes characteristic of a Fe-rich phase was observed.

No magnetoresistance (MR) was observed in the pressed Co-Cu and FeCo-Cu core-shell nanoparticles. The MR property was observed in the pressed Co-Au core-shell nanoparticle pellets. The core-shell nanoparticle pellets follow a metallic conduction behavior even with the presence of the surfactant. MR had a maximum value when the sample was annealed at 200 °C and decreased with an increase of annealing temperature. The increased particle size and the intraparticle interaction are responsible for the GMR change.
The electrochemical reaction was characterized with a polarization curve and used to estimate the reaction rate in aqueous solutions between the cobalt/iron nanoparticle and the copper electrolyte solution and was found to be similar: 0.0015 A/cm² and 0.0022 A/cm² for the Co-Cu and Fe-Cu systems. Hence, a factor other than the reaction rate must be contributing to the partial versus complete displacement of the core. It has been suggested that the porosity arising from the lattice mismatch between the shell and the core is a contributing factor. In order to further summarize the behavior a preliminary model is presented.

8.2 Model Summary

In an excess of copper ions, the cobalt nanoparticle was found to be a self-limiting reaction and the formed copper shell inhibited further reaction between the cobalt core and the copper ions, while, the iron nanoparticle was completely displaced with copper ions and formed a solid copper nanoparticle without the core-shell nanoparticle formation. Thus, the Cu shell may be most porous when formed onto a Fe nanoparticle. The reaction between the FeCo nanoparticles and the copper ions represents an intermediate case. A summary of these results is presented here using a conventional macroscopic shrinking core model.

8.2.1 Assumptions
(1) Co and Fe nanoparticles are assumed to be non-porous spheres as supported by the TEM results in Chapter 1.

(2) The metallic Co nanoparticles were displaced by noble metal ions (A), following Equation (8.1a) to form a noble metal (copper or gold) shell as presented in Chapter 3 for
Co-Cu and Chapter 4 for Co-Au core-shell nanoparticles or to be completely sacrificed following Equation (8.1b), as described by the Fe-Cu system in Chapter 5.

\[ 2A^{m+} + (m+2)Co_{NP}(s) \rightarrow 2Co_{coreA_{shell}} + mCo^{2+} \quad (8.1a) \]

\[ Cu^{2+} + Fe_{NP}(s) \rightarrow Cu_{NP} + Fe^{2+} \quad (8.1b) \]

(3) The solution volume does not change with the reaction progress.

(4) When there is an excess of noble metal ions the pseudo-steady state assumption is used, i.e., the concentration of noble ions in solution can be thought as constant without changing with the reaction time: \[ \frac{\partial C_A}{\partial t} = 0 \]. The gold ion concentration was time dependent due to the limited amount of added gold salts.

(5) The reaction rate at the surface is only a function of the copper or gold ions and independent of the core metal ions.

(6) The densities of the cobalt nanoparticle, iron nanoparticle are considered to be equal to the bulk values.

(7) The heat of the reaction is negligible.

The above experimental observation and the assumptions make the shrinking core model (SCM) applicable to the copper or gold shell formation around the cobalt core, and the solid copper nanoparticle formation from iron nanoparticle.

### 8.2.2 Modeling Equations

#### 8.2.2.1 Continuity Equation for the Reacting Core Nanoparticle

The continuity equation for the reacting nanoparticles is given by
\[
\frac{\partial C_s}{\partial t} = -r_s \rho_s \tag{8.2}
\]

where \( C_s \) is defined as the concentration of solid, nanoparticle, expressed in \( mol \) of \( S/cm^3 \); 
\( r_s \) is the reaction rate of the nanoparticle based on the weight of the particle, \( mol \) of \( S/g.s \); and \( \rho_s \) is the density of the nanoparticle, \( g \) of \( S/cm^3 \).

The time required for the reaction front to move from the surface to a distance \( r_c \) from the center of nanoparticle is obtained by a mass balance (the generated shell equals to the amount of the diffused ions) in the reaction front:

\[
ar_s \rho_s \frac{V}{A} = D_{eA} \left( \frac{\partial C_{As}}{\partial r} \right)_{r=r_c} \tag{8.3}
\]

where \( a \) is the stoichiometric coefficient, \( C_{As} \) is the concentration of ions, expressed in \( mol \) of \( A/cm^3 \), \( D_{eA} \) is expressed in \( cm^2/s \), \( A \) is the particle surface area, \( cm^2 \) and \( V \) is the particle volume \( cm^3 \).

Substituting (8.3) into (8.2) describes the change of the solid concentration change with time by the ions that reach the particle surface

\[
- a \frac{d}{dt} \left( \frac{C_s 4\pi r_c^3}{3} \right) = D_{eA} \left( \frac{\partial C_{As}}{\partial r} \right)_{r=r_c} 4\pi r_c^2 \tag{8.4}
\]

**8.2.2.2 Continuity Equation for the Reacting Shell Ions**

The continuity equation for the noble metal ions, \( A \) is given in Equation (8.5), which contains an accumulation term accounting for the transient nature of the process, and a term arising from the effective diffusivity.
\[
\frac{\partial}{\partial t} (\varepsilon_s C_{As}) = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D_{eA} r^2 \frac{\partial C_{As}}{\partial r} \right) \tag{8.5}
\]

### 8.2.2.3 Initial and Boundary Conditions

**Initial condition at \( t=0 \):**

\[
C_{As} = C_{Ao}, \text{ and } C_S = C_{So} \tag{8.6}
\]

In the center of the particle, \( r=0 \) (for reasons of symmetry):

\[
\frac{\partial C_{As}}{\partial r} = 0 \tag{8.7}
\]

**Boundary condition at the reaction front \( r=r_c \):**

\[
D_{eA} \left( \frac{\partial C_{As}}{\partial r} \right) = \frac{i}{nF} \tag{8.8}
\]

The current density, \( i \), is determined by a Tafel expression,

\[
\frac{i}{nF} = k_o C_A \exp \left( -\alpha_e nF \frac{E}{RT} \right) \tag{8.9}
\]

where \( i \) is the current, in the unit of A, \( k_o \) is the standard heterogeneous rate constant, cm/s, \( n \) is the number of electrons involved in an electrode reaction, equiv/mol, \( F \) is the Faraday constant, C/equiv, \( \alpha_e \) is the transfer coefficient, (unitless), \( R \) is the gas constant J mol\(^{-1}\) K\(^{-1}\), \( T \) is the temperature, K and \( E \) is the potential, V.

It was reported that effective diffusivity is related to porosity \( \varepsilon_s \) and a parameter \( \beta \) by the following relation...
\[ \frac{D_{eA}}{D_{eA0}} = \left( \frac{\varepsilon_s}{\varepsilon_{s0}} \right)^\beta \]  

(8.10)

The parameter is reported within 1.5 to 3 ranges.\textsuperscript{1,2} Here, 2 was used as proposed by Brouwers et al.\textsuperscript{2}

As the reaction proceeds the porosity will decrease as the shell thickness increases, according to:

\[ \frac{\partial \varepsilon_s}{\partial t} = (\nu_s - \nu_p) \frac{i A}{nF V} \]  

(8.11)

where \( \varepsilon_s \) is the porosity, \( \nu_s \) is the shell metal molar volume, \( \nu_p \) is the core metal molar volume.

The initial porosity is constant and depends on the mismatch between the shell atomic unit cell and the core atomic unit cell arising from the lattice constant difference. Based on the unit cell, the initial porosity can be obtained by Equation (8.12):

\[ \varepsilon_0 = \frac{V_{shell} - V_{core}}{V_{shell}} = \frac{a_{shell}^3 - a_{core}^3}{a_{shell}^3} \]  

(8.12)

where, \( V \) and \( a \) are the volume and lattice constant of unit cell, respectively.

From electrochemical data in Figure 3.13 and Figure 5.3, from Chapters 3 and 5, the transfer coefficients, \( \alpha_c \) and reaction rate constants, \( k_0 \), and the diffusivity can be determined. For example for \( \text{Cu}^{2+}/\text{Cu} \) the values were calculated to be \( \alpha_c = 0.094 \), \( k_0 = 1.33 \times 10^{-5} \text{ cm}^3/\text{s/mol} \) and \( D_{eA0} = 1.265 \times 10^{-6} \text{ cm}^2/\text{s} \).
With the reported lattice constants of 0.35447 nm (Co), 0.2867 nm (Fe), 0.3615 nm (Cu), and 0.40786 nm (Au), the calculated porosity for the Co-Cu, Fe-Cu and Co-Au is 0.057, 0.5 and 0.343, respectively, and is summarized in Table 8.1.

**Table 8.1 Parameters for the Equation**

<table>
<thead>
<tr>
<th></th>
<th>Initial radius (nm)</th>
<th>Lattice constant (nm)</th>
<th>Electrolyte solution (M)</th>
<th>Initial porosity*</th>
<th>Change of molar volume (cm$^3$/mol)</th>
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<tr>
<td>Co/Cu</td>
<td>3.1</td>
<td>0.35477/0.3615</td>
<td>0.25</td>
<td>0.057</td>
<td>0.46</td>
</tr>
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<td>0.35477/0.40786</td>
<td>0.024</td>
<td>0.343</td>
<td>3.559</td>
</tr>
<tr>
<td>Fe/Cu</td>
<td>6.2</td>
<td>0.2867/0.3615</td>
<td>0.25</td>
<td>0.5</td>
<td>0.0155</td>
</tr>
</tbody>
</table>

* From Equation (8.11)

Equations (8.1-8.12) summarize the behavior of the different metal displacement reactions. The core decreases according to Equation 8.4 as the reaction with the noble metal progresses, Equation 8.4 and the reactant is replenished at the surface, Equation 8.8. In the case of the Co-Cu core-shell nanoparticles, the small porosity in the Co-Cu system will increase the resistance of diffusion of the copper ions into the copper shell. As the reaction time progresses, the porosity will decrease according to Equation 8.11. Inspecting the coefficient on the right hand side of the equation can be used to compare how fast the porosity will change compared to the other systems, since the reaction rates ($i/nF$) are comparable. Table 8.1 shows that for the Co-Cu system the difference in the molar volumes is largest so that both a small initial porosity coupled with a large molar volume
change will lead to a rapidly decreasing porosity and a self-limited reaction. On the other hand, the lattice mismatch between iron and copper is largest, suggesting a large initial porosity. The difference between the molar volumes of the copper and iron is smallest which also contributes to the slow change in the porosity. In agreement with the data, the porosity remains so large that the core is completely displacement before the porosity decrease to zero. A similar problem is encountered with the Co-Au system, but to counteract the complete dissolution of the Co core the gold ions are limited in the solution. The same could be done with the Fe-Cu system, (limit the amount of Cu(II) ions), however, this would lead to an extremely porous shell and would be expected not to be stable in air.

8.3 Future Work

An outline of a macroscopic model to predict whether a noble metal coupled to an oxidizable core has been presented and can be used to assess other potential core-shell systems. The model can also be used to track the change of the nanoparticle size with time and may be the subject of future work. A weakness of the model is that it neglects molecular scale features so cannot simulate the structure of the shell.

Another area of interest is in varying the ratio of the core size to the shell thickness which should change the magnetic property and the subsequent magnetoresistance. This project is rather challenging since the type of surfactant dictates the core size and the displacement reaction kinetics and diffusivity gives an inherent shell size.

Applications of the core-shell nanoparticles require the self-assembling of the nanoparticles in a 2-D or 3-D structure for magnetic data storage. The core-shell
nanoparticles can also be used in optical magnetic resonance imaging (MRI) and biological detection when the surface of the nanoparticles is functionalized. Functionalization may be accomplished as a post-treatment step of synthesis and would need to be compatible with surfactant that is retained on the nanoparticle. The compatibility of the surfactant and solvent would play a role in functionalization of the nanoparticle such as the solubility of the surfactant in the solvent.

8.4 Reference


Appendix: Letter of Permission

From: Zhanhu Guo [zguo1@lsu.edu]
Sent: Wednesday, June 22, 2005 11:51 AM
To: Terry McCloughan
Cc: nanomaterials2000@gmail.com
Subject: J. Electrochem. Soc. -- Permission of reprint for manuscripts

Dear Sir or Madam,

I am writing to apply for the permission to reprint my published manuscript, published in JES, in my dissertation.


If you have further questions, please don't hesitate to call me at (225)-578-4895 or (225)-288-1186. If approved, please either email or fax the permission to me at (225)-578-1416. Thank you in advance for your considerations.

Sincerely yours,

Zhanhu Guo
Gordon A & Mary Cain Department of Chemical Engineering,
Louisiana State University,
Baton Rouge, LA, 70803
Phone: 225-578-4895 (Lab) Fax (225) 578-1476
Email: zguo1@lsu.edu

Permission is granted to include the above-referenced paper in your thesis, provided that you obtain permission of the other individual authors. In the thesis, please acknowledge the authors and the citation given above, and include the words: "Reproduced by permission of The Electrochemical Society, Inc."

5 July 2005

Mary E. Yess, Deputy Executive Director

6/22/2005
VITA

Mr. Zhanhu Guo was born in YunCheng, ShanXi Province, on October 18, 1973, the son of Wenzhi Guo and Guirong Tan. Mr. Guo has two elder brothers and 4 elder sisters. Mr. Guo received his Bachelor of Science from ShanDong Institute of Mining & Technology (currently Shandong University of Science & Technology, SUST) in 1996 and his Master of Science degree from Beijing University of Chemical Technology (BUCT) in 1999. Mr. Guo worked for one year in Beijing Research Institute of Chemical Industry (BRICI) as an Associate Engineer. Mr. Guo joined the doctoral program at Louisiana State University (LSU) in August 2000 and obtained a non-thesis Master of Science Degree in May 2004. Mr. Guo, a doctoral candidate, will receive the degree of Doctor of Philosophy at the December 2005 Commencement. All the above degrees are and will be from chemical engineering.