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Size control and characterization of colloidal magnetic cobalt nanoparticles

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SIZE CONTROL AND CHARACTERIZATION OF COLLOIDAL MAGNETIC
COBALT NANOPARTICLES

A Thesis

Presented to

The Faculty of the Department of Chemical and Materials Engineering

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Abhishek Singh

August 2008

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ABSTRACT

SIZE CONTROL AND CHARACTERIZATION OF COLLOIDAL MAGNETIC COBALT NANOPARTICLES

by Abhishek Singh

The overall goals of this research were to synthesize magnetic cobalt nanoparticles and characterize their structural and magnetic properties. Cobalt nanoparticles were synthesized via high temperature reduction of cobalt chloride utilizing two different surfactants, tributylphosphine and trioctylphosphine, and varying the surfactant-to-reagent molar concentration for each. X-ray diffraction results indicate that each synthesis condition yielded nanoparticles with an ϵ -cobalt crystal structure, a resemblance to the β -manganese structure. Transmission electron micrographs indicate the formation of discrete hexagonal networks among the particles with inter-particle spacing of 2-5 nm. Sizing analysis found that utilizing a bulkier surfactant yields smaller mean particle size. Furthermore, utilizing a surfactant at a higher surfactant-to-reagent molar ratio also yields a smaller mean particle size with a tighter distribution. Normalized vibrating sample magnetometer results indicate synthesized cobalt nanoparticles exhibit ferromagnetic behavior at room temperature and increasing coercivity with mean particle size.

To my parents, Dharam and Yashodhara, my family, friends, and all of my teachers,

Thank you for loving, caring, educating, and inspiring.

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CHAPTER ONE: INTRODUCTION

1.1 The Promise of Nanotechnology

Nanotechnology is defined as a field of technology in which the goal is to control individual atoms and molecules to create materials and products which are thousands of times smaller than current technologies [1]. Nanotechnology encompasses dimensions of 100 nanometers and smaller. Materials at the nanoscale give rise to unique structural, geometric, and magnetic properties. These unique size-dependent properties have been the major driving force for the study of mono-dispersed nanoparticles in the fields of microelectronics, data storage, and medicine. In the near future nanotechnology could make a supercomputer so small it could barely be visible in a microscope [2]. Medical nanorobots could navigate our bodies eliminating bacteria, alleviating clogged arteries, and reversing the effects of old age [2]. Low cost solar cells and batteries could replace coal, oil and nuclear fuels with clean, cheap, and abundant solar energy [2]. Today, governments, corporations, and venture capitalists worldwide spend more than \$8.6 billion on nanotechnology research and development [2]. The U.S. government has appropriated more than \$3.16 billion since 2000 and continues to allot over \$1 billion annually for this field of research [2].

The applications for magnetic nanotechnology are vast including data storage, DNA sequencing, drug delivery, biomedical sensors, magnetic resonance imaging, radiation therapy, nanoelectronics, military weapons and defense. An example is the utilization of magnetic nanoparticles in cancer treatment. Hysteresis is the result of magnetized remnants that persist after an applied magnetic field is removed. Each cycle

of applying a magnetic field generates a hysteresis loop, which has an associated energy loss proportional to the area of the hysteresis loop [2]. Magnetic nanoparticles with an effective coercivity can be utilized at a cancerous site in the body. Application of an alternating magnetic field will result in selective warming at the cancerous site due to hysteretic energy loss [2]. This increase in temperature can be used to increase the effectiveness of chemotherapy and radiation based therapies [2]. However, without a set of uniformly sized nanoparticles it is difficult to control hysteretic energy dissipation, which could result in collateral damage to surrounding cells and organs.

Current research has shown that solution-based high-temperature synthesis based on oxidation-reduction of a metallic salt is the predominant method for synthesizing mono-dispersed cobalt nanoparticles [3, 4]. This technique involves the addition of reagents into a homogeneous solvent at elevated temperatures, which serves to provide discrete nucleation sites and allow for size control [3]. The resultant nanoparticles are uniform in size and composed of an inorganic crystalline core surrounded by an organic monolayer, which prevents oxidation and conglomeration of the nanoparticles [3]. Recent studies have shown results of cobalt nanoparticles ranging in size from 5-30nm with standard deviations of 5-15% [3,4,5]. To alter size and size distribution of the nanoparticles current research has suggested varying reaction time, reaction temperatures, variation of organic surfactant, and varying molar ratios of surfactant-to-reagent [3]. Of these variables, current research has indicated that the organic surfactant and the ratio of surfactant-to-reagent have the best potential for controlling the size and distribution of the resultant nanoparticles [3].

Characterization is critical to ensure that the synthesis procedure is yielding nanoparticles of the desired size and distribution. Physical characterization of magnetic nanoparticles includes x-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD identifies the crystallographic structure of the nanoparticles [6]. A transmission electron microscope is utilized to capture images of the magnetic nanoparticles, subsequently utilized for sizing and distribution analysis.

Magnetic analysis is critical for complete characterization of magnetic nanoparticles. In this study, magnetic analysis will be conducted using a vibrating sample magnetometer (VSM). The VSM generates voltage readings which are proportional to the magnetization and volume of the sample [7].

The focus of this study was to characterize mono-disperse magnetic cobalt nanoparticles synthesized using two surfactants, with differing size side alkyl chains, at two surfactant-to-reagent molar ratios. XRD was utilized to determine elemental composition and crystallographic structure and TEM for size and size distribution analysis. VSM will be used to capture the magnetic properties of the synthesized nanoparticles.

1.2 Significance

The applications and utilization of magnetic nanoparticles and nanotechnology is a vast field of opportunity. However, in order to make use of magnetic nanoparticles into a viable product, characterization to a high level of precision and accuracy is necessary to understand their size-dependent properties. For all nanoparticle applications, magnetic or otherwise, it is critical to be able to control physical properties such as size, structure,

shape, and self-assembly. For magnetic nanoparticle applications, it is further necessary to characterize magnetic properties including saturation magnetization, coercivity, and hysteretic behavior. Only when these properties are characterized and demonstrated repeatedly can magnetic nanotechnology become viable on an industrial scale.

CHAPTER TWO: LITERATURE REVIEW

2.1 Nanoparticle Synthesis Methodologies

2.1.1 Top-down versus Bottom-up Approach

Synthesis of nanoparticles can be accomplished by two approaches: top-down and bottom-up. In top-down synthesis, a bulk starting material is attenuated physically or chemically to the desired dimensions. This approach is utilized in the semiconductor industry to form electronic devices on silicon substrates via deposition of bulk films, photolithographic patterning, and reactive etching [8]. A second example of top-down synthesis of nanoparticles is ball-milling, where nanoparticles are created through controlled mechanical degradation of a bulk starting material [8]. This technique is utilized by the cosmetics industry for producing items such as lotions and powders. The primary advantages of top-down synthesis are low cost and high volume manufacturing capability. However, for most nanoparticle synthesis applications top-down synthesis is difficult to employ because of controllability issues in size and shape, hence it is not used very often [8]. In the bottom-up synthesis approach, atoms and molecules are synthesized into nanoparticles by induced self-assembly, which are then used to build nanostructures [8]. An example of bottom-up approach is the synthesis of titanium oxide (TiO₂) nanoparticles via hydrolysis of titanium tetrachloride (TiCl₄) as shown in Equation 1 [8].

In the case of microelectronics fabrication, both synthesis approaches are utilized in order to achieve a final product. In general, the degree of control necessary in order to

achieve desired nanoparticle dimensions dictates the synthesis approach. For the case of magnetic nanoparticles, size and size distribution is of utmost importance in order to produce key size-dependent structural and magnetic properties, hence a top-down approach is not applicable. The work of Murray [5] has shown that a solution-based bottom-up synthesis approach is the best technique for synthesis of uniform cobalt nanoparticles.

2.1.2 Bottom-up Synthesis: Thermal Decomposition of Organometallic and Polymer Compounds

One bottom-up synthesis technique is thermal decomposition of organometallic or polymer compounds. This technique has two available routes for synthesis. In one, an organometallic or polymer compound is reacted with a reducing gas, either hydrogen or carbon monoxide to yield ligand-free zero-valent metal nanoparticles. In the other route, a metal-carbonyl precursor is reacted with trioctylphosphine oxide (TOPO) and oleic acid at elevated temperatures to yield metal nanoparticles, as shown in Figure 1 [9]. These routes of synthesis follow a simpler process, relative to thermal oxidation-reduction, and can be integrated to larger scales with ease, however, they yield nanoparticles which are relatively inconsistent and non-uniform in shape, show relatively larger size distributions compared to thermal oxidation-reduction, and have limited yield with select metals [9]. The work of Sowka et al. for example shows that thermal decomposition of a cobalt acrylamid complex yields irregular powder particles which range in size from 10 to 300 microns [9,10]. For applications of magnetic nanoparticles, this range in particle size would yield differing magnetic properties, hence making a product virtually impossible to manufacture with this technique.

Figure 1. Thermal decomposition of organometallic precursor to nanoparticles.

2.1.3 Bottom-up Synthesis: Reduction of Metal-Salts

A more feasible route for synthesis of magnetic nanoparticles is high-temperature (100 – 300 °C) solution phase reduction of metal salts, which yields a colloidal suspension of metal nanoparticles. This route is based on a temporally discrete nucleation event which is followed by relatively rapid growth from solution phase atoms to nanoparticles and subsequent slower growth of the nanoparticles by Ostwald ripening [5,11]. Specifically in this synthesis technique, a metal salt is dissolved to supersaturated levels in organic coordinating solvents at approximately 100 °C. Thereafter, a surfactant is added to the solution with its purpose being to homogenize the solution and stabilize nanoparticles upon nucleation [5]. Nucleation is induced rapidly by ramping up the temperature of the solution to 210 °C and injecting a strong reducing agent [5]. A temperature greater than 200 °C is necessary to drive the reduction reaction. The nucleation process proceeds until the ionic metal species falls below the critical concentration for nucleation. The nucleated atoms grow into nanoparticles and Ostwald ripening of the nanoparticles then follows. Growth of the nanoparticles can be terminated by limiting the amount of time that the solution is held at 210 °C. Upon achieving the

desired nanoparticle size, cooling the solution to room temperature halts any further reaction phenomena [5]. Figure 2 displays the basic reaction.

Figure 2. Reduction of a metal-salt to metal nanoparticles.

The nucleation burst is very short, lasting on the order of 40 seconds [11]. During this first stage, size distribution remains relatively narrow [11]. The nucleation stage is then followed by slower growth via Ostwald ripening, where smaller nanoparticles shrink and eventually dissolve in favor of growth of larger nanoparticles [11]. La Mer's studies have found that the size distributions become broader during the Ostwald ripening stage, primarily because Ostwald ripening is not uniform throughout the solution. By controlling the exposure time of the solution at peak temperature, this synthesis technique yields mono-disperse nanoparticles which have a crystalline metallic core coordinated by an organic monolayer as shown in Figure 2 [5].

The work of Murray et al. has shown that the reduction of cobalt acetate tetrahydrate in diphenylether stabilized by trioctylphosphine, yields cobalt nanoparticles tunable from 1-15 nanometers (nm) in size with a standard deviation of less than 5% [5]. Similarly the work of Su et al. shows the reduction of cobalt chloride in diphenylether stabilized by triphenylphosphine, yields cobalt nanoparticles with an average size of 9 nm with a standard deviation of 7% [3]. The work of Zhao et al. also shows that reduction of

cobalt chloride in ethanol and mineral oil solutions yields nanoparticles of 4.7 nm on average with a standard deviation of 1.6 nm [12]. The work of Zhao et al. shows the smallest average particle size; however it should be noted that the standard deviation in size is also the greatest. In the experimental work conducted by Zhao et al. a stabilizing agent was not used, rather, nucleation and growth were controlled by immediately transferring formed particles out of solution and further reaction. This transfer process is limited in precision and is the most likely explanation for the large standard deviation in nanoparticle size.

In synthesis of magnetic nanoparticles via the reduction of metal salts, variation of the reaction conditions such as time, temperature, and concentration and type of reagents and surfactants can be used to control nanoparticle size [5]. In general, nanoparticle size increases with increasing reaction time and with increasing temperature; however, these are not preferred tuning parameters for scale-up to mass production levels [5].

Based on the work of Murray et al. and Su et al., the choice of surfactant and molar ratio of surfactant-to-reagent are the preferred tuning parameters to control nanoparticle size [3,5]. Choice of surfactant allows for the utilization of steric effects. Steric effects arise due to the fact that different atoms and molecules occupy a different amount of space. During post-nucleation nanoparticle growth, the surfactants in solution adsorb reversibly to the surfaces of the nanoparticles, resulting in an organic monolayer shell that surrounds and stabilizes the nanoparticles in solution and restricts their growth [5]. Larger and bulkier surfactant molecules which bind more tightly to the nanoparticle

surface provide greater steric hindrance to the solution surroundings. This serves to slow the rate of material addition to the encapsulated nanoparticle nuclei, resulting in smaller average nanoparticle size [11]. Utilizing a larger ratio of surfactant-to-reagent serves to provide more readily available surfactant molecules for each nucleated nanoparticle.

Murray et al. have suggested that increasing the surfactant-to-reagent concentration leads to an increase in coordination between nanoparticles [5]. This increase in coordination yields the formation of a greater number of smaller initial nuclei, which are resistant to growth [5, 13].

Su et al., utilizing UV-Visible absorption method, found a shift in the maximum absorption peak, when the ratio of triphenylphosphine-to-cobalt (surfactant-to-reagent) increases, indicating a decrease in nanoparticle diameter [3]. The UV-Visible absorption method does not yield accurate average particle sizing data, however, it is an excellent method for initial process screening for formation of nanoparticles. The work of Murray et al. suggests that using the bulkier trioctylphosphine surfactant versus tributylphosphine yields a smaller average nanoparticle size. The work of Yang et al. states that the phenyl groups in triphenylphosphine can provide greater steric hindrance compared to straight-chained alkyl groups such as tributyl and trioctyl to control size of nanoparticles [13].

The experimental work of Yang et al. yielded an average nanoparticle size of 7 nm with a size distribution of approximately 5% [13]. The work of Thanh et al. suggests the use of peptide capping ligands on cobalt nanoparticles for use in biomedical applications.

Thanh et al. state that peptides chosen with appropriate structural and functional groups serve to control the nucleation and growth processes to produce desired morphology and

internal structure of nanoparticles [14]. Most studies have suggested that varying the type of surfactant and its relative concentration is an excellent way to engineer nanoparticle size; however, a single experiment utilizing different surfactants and different relative concentrations has not been presented, hence a direct comparison is needed to provide confirmation.

2.1.3.1 Isolation of Synthesized Nanoparticles

Completion of synthesis via the reduction of a metal-salt yields a colloidal suspension of metal nanoparticles encapsulated by an organic monolayer. The solvent in which the nanoparticles are suspended is largely an organic waste by-product. For characterization, isolation of the nanoparticles from the waste by-product is critical. Isolation techniques employed by many researchers include decantation, centrifugation, filtration, or a combination of the above followed by polar and non-polar solvent washes. The washes serve to remove residual organic waste and upon completion, the nanoparticles are re-dispersed in a non-polar solvent. In their synthesis of cobalt nanoparticles, Zhao et al. decanted the supernatant and then proceeded to wash the remnants with ethanol, acetone, and deionized water [12]. Respaud et al. utilized filtration to isolate cobalt nanoparticles, which were then re-dispersed in a mixture of tetrahydrofuran and dichloromethane [15]. The imaging results of Respaud et al. were of low quality when compared to the work of others and it is suspected that the filtration technique utilized for isolation may be the cause. Sun et al. utilized a combination technique: first decanting the supernatant, dispersing in a non-polar solvent, then centrifuging followed by another decanting, and dispersion [16]. Su et al. similarly

utilized a centrifuge, then decanted the supernatant, and followed by re-dispersing the nanoparticles in heptane [3]. Lisiecki et al. in their work decanted the supernatant, and then utilized a series of centrifuge cycles to isolate different sizes of nanoparticles [17]. Based on results seen thus far, a combination of decantation, polar and non-polar solvent washes, centrifugation, followed by re-dispersion in a non-polar solvent yields a magnetic nanoparticle colloidal suspension which is optimal for characterization.

2.2 Structural Characterization

There are many routes in the synthesis of nanoparticles. The results of many experiments have shown that bottom-up synthesis based on the reduction of metal-salts is the easiest and most widely used method for preparation of uniform sized metal nanoparticles [9]. Parameters of importance in structural characterization include: size, shape, dispersion, elemental identification, and crystallographic structure. X-ray diffraction (XRD) and transmission electron microscopy (TEM) are two techniques, of many, which are consistently utilized for such characterization purposes.

2.2.1 X-Ray Diffraction (XRD)

Diffraction can occur when electromagnetic radiation interacts with a periodic structure whose repeat distance is about the same as the wavelength of the radiation [18]. X-ray wavelengths are on the order of angstroms, in the range of typical interatomic distances in crystalline solids. Therefore, X-rays can be diffracted from the repeating patterns of atoms that are characteristic of crystalline materials, yielding information on crystal structure [18].

Consider an X-ray beam incident on a pair of parallel planes, Plane 1 and Plane 2, separated by an interplanar spacing, d , as shown in Figure 3.

Figure 3. X-ray diffraction reflection geometry.

The two parallel incident rays A and B make an angle θ with planes P1 and P2. A reflected beam of maximum intensity will result if the waves represented by A' and B' are in phase, which occurs when the difference in path length between A to A' and B to B' is an integral number of wavelengths, λ [19,20]. Interaction of X-rays with a sample creates diffracted beams of X-rays related to interplanar spacing in the crystalline materials according to Bragg's Law, Equation 2 [20].

$$n\lambda = 2d \sin \theta \quad \text{Equation 2}$$

In Equation 2, n is an integer, λ is the wavelength of the X-rays, d is the interplanar spacing, and θ is the diffraction angle. In X-ray diffraction analysis, the wavelength, λ , is known, and the diffraction angle, θ , is measured. Utilizing Equation 2, the interplanar spacing, d , can be calculated. Utilizing diffraction data for different planes the unit cell can be completely mapped. The intensity of the diffraction maximum

is also recorded and is related to the strength of those diffractions in the specimen [21]. The intensities of the diffraction maximums are determined by the distribution of the electrons in the unit cell. The highest electron density is found around atoms and so the intensities can be utilized to determine what kind of atoms are present and where in the unit cell they are located [21]. Identification of an element or compound and its crystal structure is accomplished by comparing the measured intensity data from a specimen with peaks and relative intensities from a very large set of standard data provided by the International Center for Diffraction Data (ICDD) and through use of various database software packages.

The work of Sowka et al. utilized XRD for change in structure of cobalt nanoparticles synthesized via thermal decomposition of a polymer complex. Sowka et al. used XRD patterns to understand the mechanism of thermal decomposition of the polymer complex leading to the formation of cobalt nanoparticles [10]. Elemental cobalt has two known crystal structures at ambient pressures, hcp and fcc. Bulk hcp structure is stable at temperatures below 425 °C while bulk fcc is the stable structure at higher temperatures [5]. XRD results from Sun and Murray yielded cobalt nanoparticles, which are neither hcp nor fcc. Utilizing relative intensities and interplanar spacing data shown in Table 1, Sun and Murray were able to prove cobalt nanoparticles have a third phase (ϵ -Co) which matches with the symmetry of the β phase of manganese [16]. This crystal structure is a complex form of the primitive cubic cell with 20 atoms within at unequal separation distances [16].

Table 1. Diffraction comparison of 11 nm cobalt nanoparticles and β phase of manganese [16].

d-Co (Å)	Relative Intensity	d-Mn (Å)	Relative Intensity	hkl
2.73	5	2.823	5	210
2.49	4	2.577	5	211
2.16	8	2.231	7	220
2.04	100	2.104	100	221
1.94	56	1.997	60	310
1.85	31	1.904	25	311
1.63	9	1.6872	9	321
1.44	7	1.4874	6	330
1.37	7	1.4115	5	420
1.2	23	1.2377	25	510
1.13	18	1.1721	20	520

For an infinitely large single crystal, XRD will yield a single line in the diffraction pattern. However, for nanoparticles XRD patterns will yield broader peaks because the reciprocal lattice is based on an inverse length scale and so as particle size decreases the pattern width increases [21]. The work of Shevchenko et al. utilized XRD to show the variation in diffraction pattern as a function of nanoparticle size [22]. Shevchenko et al. found that the peak width at half-maximum intensity nearly tripled as CoPt₃ nanoparticle size decreased from 5.5 nm to 1.5 nm. Many researchers have utilized XRD peak widths at half-maximum intensity to determine approximate shifts in nanoparticle size with further refined sizing data captured via transmission electron microscopy.

2.2.2 Transmission Electron Microscopy (TEM)

In a transmission electron microscope, a high-energy electron beam is transmitted through a very thin sample to image and analyze the microstructure of materials at atomic scale resolution [23]. Electrons are emitted from an electron gun and illuminate the

specimen through a two or three stage condenser lens system. An objective lens provides the formation of either image or diffraction pattern of the specimen [23]. The electron intensity distribution behind the specimen is magnified with a three or four stage lens system and viewed on a fluorescent screen [23]. An image can be recorded by direct exposure of photographic film or via an attached digital camera.

The image of a specimen in a transmission electron microscopy is formed selectively allowing only the transmitted beam, known as bright-field imaging, or one of the diffracted beams, referred to as dark-field imaging, down the microscope column through an aperture [23]. The electrons are accelerated anywhere from 30-400 hundred kV, yielding wavelengths which are smaller than that of visible light and X-rays. The electron microscope, however, is limited by aberrations inherent in electromagnetic lenses, and hence imaging resolution is limited to about 1-2 Angstrom [23].

Sample preparation for TEM in general requires the most time, experience, and sensitivity compared to most other characterization techniques [23]. A TEM specimen must be approximately 1000 Angstrom or less in thickness in the area of interest. The entire specimen must fit into a 3 mm diameter grid. For analysis of nanocolloidal solutions there are several techniques for sample preparation including: grid submersion, solution spray method, vacuum evaporation, and eye-drop heated evaporation [3,4,5,24]. In grid submersion, a TEM grid is submerged into the nanocolloidal solution for a short period of time, followed by a slow drying period for the solvent to evaporate. The work of Su et al. suggests placing the TEM grid in a covered Petri dish after submersion to slow the drying rate of the solvent [3]. Su et al. indicate that slowing the drying rate

prevents conglomeration of the nanoparticles on the grid [3]. The solution spray method utilizes a fine mister to apply a small volume of nanocolloidal solution to a grid. Vacuum evaporation utilizes a low-level vacuum to evaporate solvent after submersion of a TEM grid. In the eye-drop heated evaporation technique an eye-drop volume of solution is applied to a TEM grid and then evaporated using a heater. Use of a nebulizer to create a fine aerosol mist after a sample has been exposed to sonic vibrations has been suggested as the best preparation technique for nanocolloidal samples [25].

2.3 Magnetic Analysis

To characterize magnetic nanoparticles and understand their properties, geometric and structural analysis must be complemented with magnetic analysis [26]. In specific, capturing parameters such as magnetic moment, saturation magnetization, remnant magnetization, coercivity, and hysteretic behavior is critical for understanding the nature of these particles and absolutely necessary if their properties are to be exploited for application purposes.

2.3.1 Vibrating Sample Magnetometer (VSM)

Figure 4 shows a schematic of a vibrating sample magnetometer (VSM). A VSM contains a variable electromagnet, which provides the magnetic field, detection coils, which capture the flux emerging from a specimen, a non-magnetic rod where the specimen is mounted, and a vibration unit which serves to vibrate the specimen [7,27].

Figure 4. VSM Schematic

The specimen is mounted at the end of the nonmagnetic rod and vibrated via the vibration unit, using either a loud speaker or modified voice coil motor, at a nominal frequency [7]. A VSM works on the principles of Faraday's Law of Induction, which states that an electric field is produced by a changing magnetic field. In a VSM, the sample is placed in a magnetic field resulting in the sample being magnetized, hence, having its own magnetic field. The larger the applied field, the greater the magnetization. In order to detect the magnetization, a change in the magnetic field is necessary. Hence, the sample is vibrated, causing its magnetic field to change under the applied field, which generates an electric field that is proportional to its magnetization. The magnetic field (H) of the electromagnet is varied to capture the materials magnetization (M). The output result displays the magnetic moment, M , as a function of the applied field, H .

2.3.2 Hysteresis

Magnetostatic energy is defined as the energy associated with the magnetization vector, M , in the presence of an applied magnetic field, H , and is mathematically stated in Equation 3 [7].

$$E'_{ms} = - \int (M \bullet H) dv \quad \text{Equation 3}$$

Hysteresis is a property of systems that do not instantly react to external forces applied upon them and do not return completely to their original state [28]. More simply, the state of hysteretic systems depends on the path utilized to reach that particular state [7]. Hysteresis behavior is well known in ferromagnetic materials such as iron, cobalt, nickel. When an external magnetic field, H , is applied to a ferromagnet, it absorbs some of the external field by alignment of the magnetic moments with the applied field. Upon removal of the external field the magnet will retain some field: it is magnetized [28].

The relationship between the applied magnetic field, H , and magnetic moment, M , is not linear in ferromagnetic materials such as iron, cobalt, and nickel. For example, results from VSM analysis yields plots of M versus H . this plot shows for linearly increasing the magnetic field, H , the magnetic moment, M , will follow a curve up to a point where further increasing the field will yield no additional change in magnetic moment, M , indicating a state of magnetic saturation. If the magnetic field is then reversed, the magnetic moment, M , will follow a similar curve, however, offset from the original curve by an amount called the remnant magnetization. The cause of the offset is because ferromagnetic materials retain some of the induced magnetization and this has to be overcome each time the applied field across the material reverses [28]. Hysteresis

plots are utilized to extract parameters such as saturation magnetization (M_s), remnant magnetization (M_r), coercivity (H_c), shape anisotropy, hysteretic square-ness, coercive square-ness, and energy loss of a material. In Figure 5, M_s , M_r , H_c within a hysteresis loop are highlighted.

The work of Yang et al. utilized magnetic characterization to capture the change in coercivity with change in size of cobalt nanoparticles, a reproduction of which is shown in Figure 5.

Figure 5. Reproduction of Yang et al. M vs. H hysteresis loops for 6 and 9.5 nm ϵ -Co nanoparticles.

The results of Yang et al. shown in Figure 5 show an increase in coercivity with size with actual results of coercivity being 247 and 838 Oersteds (Oe) for the 6 and 9.5 nm ϵ -Co nanoparticles, respectively [13]. The magnetic characterization work of Sun and Murray reports a coercivity of 500 Oe for 9 nm ϵ -Co nanoparticles, showing temperature-based decay of coercivity. The work of Yang et al. has also shown data that samples of synthesized cobalt nanoparticles show no hysteresis behavior at temperatures above 250 K. From the work of Yang et al. hysteresis behavior is observed at a

temperature of 10 K. These results show that hysteresis behavior disappears with increasing temperature, indicating superparamagnetic behavior of ϵ -Co nanoparticles at temperatures as low as 250 K. Chiriac et al. performed room temperature VSM analysis and a reproduction of their result is shown in Figure 6. This work corroborates the work of Yang et al. in terms of the absence of hysteresis behavior, above 250 K. Chiriac et al. have reported saturation magnetization values of 121 emu/g for cobalt nanoparticles.

Figure 6. Room temperature M vs. H for cobalt nanoparticles.

The work of Respaud et al. utilized hysteresis data to show an increase in magnetic anisotropy and mean magnetic moment per cobalt atom, relative to bulk hcp and fcc phases, with decreasing nanoparticle size [15]. They speculate that surface effects and nanoparticle imperfections are the critical reason for this observed phenomenon [15]. However, the work of Hormes et al. states the changes in magnetic anisotropy and mean magnetic moment are more closely related to the nanoparticle interaction with the organic capping layer [29].

2.4 Summary

In order to exploit magnetic nanoparticles for applications, understanding and ability to manipulate the synthesis process, verified by structural and magnetic characterization, is of utmost importance. Magnetic nanoparticles have the potential for many applications including: data storage, nanoelectronics, bio-medical, and military. Being able to control their geometric and magnetic properties will allow custom tailoring to satisfy the different requirements of potential applications. Bottom-up synthesis via reduction of metal-salts has shown to be the easiest and most reliable technique to synthesize magnetic nanoparticles. Studying the effect of different surfactants and concentration values relative to reagents has been suggested as a strong method to control size and size distributions. Utilizing X-ray diffraction (XRD) and a transmission electron microscope (TEM), size, shape, and crystal structure can be evaluated and the effects of the synthesis process manipulation can be observed. A vibrating sample magnetometer (VSM) can measure changes in magnetization due to a varying applied field and provide hysteresis behavior from which magnetic parameters can be extracted. The present work focuses on these studies, so that the potential for magnetic cobalt nanoparticles and their applications can become a reality.

CHAPTER THREE: EXPERIMENTAL METHODS

3.1 Research Objectives

The overall goals of this research were to synthesize magnetic cobalt nanoparticles and characterize their structural and magnetic properties. The first objective was to demonstrate that average nanoparticle size can be controlled by the choice of surfactant. The second objective was to show that the molar ratio of surfactant-to-reagent can be utilized to control size distribution. Cobalt nanoparticles were synthesized via high temperature reduction of cobalt chloride utilizing two different surfactants, tributylphosphine and trioctylphosphine, and varying the surfactant-to-reagent molar concentration in each case. X-ray diffraction and transmission electron microscopy was utilized for identification of cobalt presence and statistical analysis of nanoparticle size data, respectively.

The third objective was magnetic analysis of the synthesized cobalt nanoparticles. A vibrating sample magnetometer was utilized to analyze magnetic behavior and to extract magnetic parameters including remnant magnetization, saturation magnetization, coercivity, hysteretic square-ness, and coercive square-ness for each synthesis condition.

The fourth objective was to develop sample preparation methods for transmission electron microscopy, x-ray diffraction, and vibrating sample magnetometry analysis. TEM samples required deposition of a colloidal sample onto a TEM grid for analysis. XRD and VSM analysis required the deposition of nanoparticle product onto a silicon substrate.

All of the research objectives were successfully met.

3.2 Research Justification

Literature has suggested that variation in choice of surfactant used in synthesis can yield a resultant variation in size, with bulkier surfactants yielding smaller nanoparticles [3,5,11,13]. Literature has also suggested that increasing the ratio of surfactant-to-reagent can be utilized to control sizing distribution in nanoparticles [3,5]. Thus far, however, there has been no formal experiment conducted in which the two parameters, type of surfactant and surfactant-to-reagent molar ratio, have been varied and the subsequent results presented.

Magnetic analysis work thus far has shown that a compensation temperature or blocking temperature exists, above which synthesized nanoparticles exhibit paramagnetic behavior and below which they exhibit hysteretic ferromagnetic behavior. Literature has also shown increases in coercivity with size [13]. Experimental work in which magnetic analysis provides saturation magnetization, remnant magnetization, coercivity, hysteretic square-ness, and coercive square-ness has yet to be conducted.

3.3 Experimental Overview

The experiments in this research were conducted based on a 2^2 full-factorial design. The design variables of this experiment are type of surfactant and surfactant-to-reagent molar ratio. Utilizing a 2^2 experimental design, two surfactants were evaluated at two different surfactant-to-reagent molar ratios, yielding a total of four unique conditions. Three trials were performed for each unique condition to prove repeatability, yielding a total of 12 synthesis runs. Table 2 summarizes the experimental conditions of this research.

Table 2. 2^2 full-factorial experimental design.

Condition	Surfactant	Surfactant-to-Reagent Molar Ratio
1	tributylphosphine	2:1
2	tributylphosphine	4:1
3	trioctylphosphine	2:1
4	trioctylphosphine	4:1

Each unique experimental condition shown in Table 2 followed an overall flow shown in Figure 7. Upon completion of synthesis of a sample, utilizing the conditions in Table 2, verification of successful formation of cobalt was acquired via x-ray diffraction. TEM analysis was then performed to verify synthesis product was cobalt in nanoparticle form. Finally, VSM analysis was completed to capture magnetic behavior. All analyses samples originate from the same synthesis batch. XRD and VSM analysis shared the same sample.

Figure 7. Experimental overview flowchart.

The experimental overview shown in Figure 7 was utilized to confirm synthesis capability, repeatability, and to collect data for all synthesis conditions listed in Table 2. Once confidence in synthesis was established, the experimental data was collected as summarized in Table 3.

Table 3. Experimental summary.

Synthesis Run	Surfactant	S:R Molar Ratio	XRD Analysis	TEM Analysis	Sizing	VSM Analysis
1	tributylphosphine	2:1	1 Sample	2 Samples	Minimum 1000 Particles	XRD Sample
2	tributylphosphine	2:1		2 Samples		
3	tributylphosphine	2:1		2 Samples		
4	tributylphosphine	4:1	1 Sample	2 Samples	Minimum 1000 Particles	XRD Sample
5	tributylphosphine	4:1		2 Samples		
6	tributylphosphine	4:1		2 Samples		
7	trioctylphosphine	2:1	1 Sample	2 Samples	Minimum 1000 Particles	XRD Sample
8	trioctylphosphine	2:1		2 Samples		
9	trioctylphosphine	2:1		2 Samples		
10	trioctylphosphine	4:1	1 Sample	2 Samples	Minimum 1000 Particles	XRD Sample
11	trioctylphosphine	4:1		2 Samples		
12	trioctylphosphine	4:1		2 Samples		

3.4 Experimental Setup

The synthesis work was carried out in the Chemical and Materials Engineering Department labs, E203 and E235, at San Jose State University. The synthesis in this research was carried out in inert atmospheric conditions due to the sensitivity of the precursor reagents to ambient conditions. The experimental setup utilized in this research was a synthesis chamber, which was isolated from ambient conditions, and an attached antechamber, which can be placed under vacuum down to -34 kPa via an attached pump. The synthesis and antechamber have gas delivery and exhaust lines to allow the flow of nitrogen gas delivered from a liquid nitrogen dewar. The synthesis chamber was utilized for all synthesis work and is accessed by an operator via a set of gloves. The antechamber serves as a load-lock chamber for insertion and extraction of equipment and

reagents necessary for synthesis, without exposing the synthesis chamber to ambient conditions. Figure 8 displays a photograph of the experimental setup for synthesis showing the synthesis chamber and attached antechamber, above which is the power module.

Figure 8. Synthesis and antechamber with power module.

XRD sample analysis was conducted at Alza Corporation and at the Materials Characterization and Metrology Center at San Jose State University. TEM sample preparation, analysis, and image development was carried out at the Department of Biological Sciences Electron Microscopy Lab, DH442, at San Jose State University. VSM analysis was conducted in the Solid State Physics Laboratory, SCI250, at San Jose State University. Table 4 summarizes the tools utilized in this research and their purpose.

Table 4. Tools summary.

Equipment	Model	Purpose
Synthesis and Antechambers	Custom	Inert synthesis environment
X-ray Diffractometer	Rigaku Ultima III PANalytical X'Pert Pro	Elemental identification, crystallography
Transmission Electron Microscope	Zeiss EM109	Particle imaging
Vibrating Sample Magnetometer	Custom	Magnetic analysis

3.5 Synthesis Method

The synthesis conducted in this experiment utilizes the inert atmospheric environment described earlier, commercially available reagents, along with commercially available glassware and equipment.

The reagents purchased from Sigma-Aldrich, Inc. included anhydrous cobalt chloride, octyl ether (99%), oleic acid (99+%), trioctylphosphine (90%), tributylphosphine (97%), lithium triethylboro-hydride (1.0 M solution in tetrahydrofuran, THF) also known as Super-Hydride®, anhydrous ethanol (99.5+%), acetone ($\geq 99\%$), and hexane ($\geq 99\%$). The glassware and equipment utilized include: Dataplate® digital hot plate/stirrer, Ohaus digital scale, clamp and stand, magnetic stir bars, gas tight syringes, 50 mL beakers, 100 mL beakers, 500 mL beakers, 225 mL flasks, 50 mL vials, graduated cylinders, eye-dropper, tongs, tweezers, scoop, petri dishes, latex gloves, and parafilm.

Prior to synthesis, all glassware utilized was cleaned with a standard soap solution followed by an acetone rinse. The cleansed glassware was then placed in an oven and dried for approximately 12 hours at 125 C. The glassware was then transferred to the

antechamber and subsequently to the synthesis chamber with minimum exposure time to ambient conditions. A typical synthesis was conducted as outlined in Figure 9.

Figure 9. Synthesis flowchart.

At room temperature within the synthesis chamber, shown earlier in Figure 8, while nitrogen gas is flowing; 0.52g (4 mmol) anhydrous cobalt chloride, 80 mL of dioctyl ether (99%), and 1.3 mL of oleic acid are added to a flask containing a magnetic stir bar. The flask is placed onto the digital hot plate/stirrer and the temperature is raised to 100 C. The stir bar is set to rotate at 350 rpm to promote good mixing. At 100 C, an organophosphine surfactant is added and the temperature is raised to 200 C. The mixture of octyl ether (99%), oleic acid, and surfactant comprise the coordinating solvent, which

serves to promote dissolution of anhydrous cobalt chloride into cobalt (Co^{2+}) and chloride (Cl^-) ions. At 200 C, Super-Hydride® ($\text{Li}(\text{C}_2\text{H}_5)_3\text{BH}$) is added which serves to reduce cobalt ions (Co^{2+}) to neutral cobalt atoms. The solution is continuously mixed and maintained at 200 C for approximately 20 minutes to allow nucleation and growth of cobalt nanoparticles. The solution is then cooled to room temperature and 25 mL of anhydrous ethanol plus a few drops of oleic acid are added to stabilize the nanoparticles in solution. The final product is a population of magnetic cobalt nanoparticles capped with an organic layer dispersed in a solution of organic by-product waste. The proposed reaction, which this synthesis technique follows, is shown in Figure 10.

Figure 10. Proposed reaction for high-temperature reduction of CoCl_2 .

The solution is then allowed to sit overnight, which allows the magnetic nanoparticles ample time to migrate to the magnetic stir-bar within the flask. The nanoparticles are then isolated based on the technique shown in Figure 11.

Figure 11. Isolation sequence flowchart.

The supernatant is decanted into a waste beaker. The supernatant is comprised of organic by-products, which hinders XRD, TEM, and VSM analysis hence it is discarded to hazardous waste for neutralization. The flask containing the magnetic nanoparticle coated stir bar is then gently rinsed with anhydrous ethanol in order to remove any bulk remnant by-product. The magnetic nanoparticle coated stir bar is then extracted from the flask, utilizing another magnetic stir bar, into a clean beaker. Hexane, via a syringe, is then used to rinse the magnetic nanoparticle coated stir bar. A syringe is utilized because a strong stream is necessary in order to remove the magnetic cobalt nanoparticles that are attracted to the magnetic stir bar. Hexane is utilized because it is a non-polar solvent, which minimizes the probability of interaction between the nanoparticles and solvent. The hexane dispersion is then washed three times with ethanol to extract as much bound organic by-products as possible. Each wash is followed by centrifugation and

decantation of the supernatant. The final product is a colloidal dispersion of organically capped magnetic cobalt nanoparticles in hexane, which is stored in a capped vial within the antechamber at reduced pressure.

3.6 X-ray Diffraction Sample Preparation and Analysis

Several methods of sample preparation were tried for XRD analysis including centrifugation, vacuum drying, and decanting. The decanting method is the simplest, where the nanoparticles are allowed to settle to the bottom of test tube and then the solvent is decanted as much as possible. However, this preparation method yields samples which have a large amount of by-products and results in XRD scans with a low signal-to-noise ratio. Vacuum drying and centrifugation are difficult because nanoparticle yield is low and these methods are not sufficiently effective to collect an isolated mass of sample which yields high-level XRD results. The best sample preparation technique was found to be deposition of the cobalt nanoparticles onto a silicon substrate via evaporation. Samples are prepared on a 25 mm² pre-cut silicon substrate, as outlined in Figure 12.

Figure 12. XRD sample preparation sequence.

The vial with the final product is shaken up to disperse any settled particles at the bottom. Twenty-five milliliters of the colloidal magnetic nanoparticle hexane solution are poured into a 50 mL beaker. Allow a few hours time for approximately 50% of the solution to evaporate yielding a smaller volume concentrated with magnetic nanoparticles. Hexane has a relatively high vapor pressure of approximately 130 mm Hg at room temperature, which allows it to evaporate quickly. Once the solution has been reduced in volume, a pre-cut silicon substrate is placed in a petri dish, which is set on the Dataplate® digital hot plate/stirrer. The digital hot plate is set to 55 C in order to allow quicker evaporation of hexane as drops of colloidal solution are placed onto the substrate. Using an eye-dropper, drops of colloidal solution are placed on the pre-cut silicon substrate. Each drop is allowed time to evaporate before the next drop is placed. Typical

evaporation time is approximately 10-15 seconds between drops yielding a rate of addition of approximately 4-6 drops per minute. This is continued until an even film of magnetic cobalt nanoparticles has been deposited on the entire pre-cut silicon substrate. The temperature is then raised to 100 C in order to drive off any remaining hexane and to “bake” the film so that it is adherent to the substrate. The sample is then sealed within a plastic container with parafilm until analysis.

At Alza Corporation, samples were scanned using a multi-array angle scanning setup in which the sample stage spins at $\frac{1}{2}$ rotation per second. Large angle range scans were performed for $2\theta = 5-110^\circ$ with a step size of 0.008. Small angle range scans were performed for $2\theta = 35-60^\circ$ with a step size of 0.004. At the Materials Characterization and Metrology Center at San Jose State University, small angle range scans were conducted for $2\theta = 40-60^\circ$ with a step size of 0.1. A scan rate of 0.05° per minute with the system in parallel beam alignment mode was utilized to acquire the best scan resolution.

3.7 Transmission Electron Microscopy Sample Preparation and Analysis

TEM sample preparation, analysis, and image development was conducted at the Department of Biological Sciences Electron Microscopy Lab, DH442 at San Jose State University. A Zeiss EM109 electron microscope, shown in Figure 13, was utilized for analysis.

Figure 13. Zeiss EM109 electron microscope.

Several techniques for TEM sample preparation were utilized in this study including: dip-method, vacuum drying, drop-method, and spray-method. In each preparation technique, a 3mm circular mesh silicon monoxide (SiO)/formvar coated TEM grid, is exposed to the colloidal cobalt suspension.

In the dip-method, the TEM grid is dipped in the solution using a pair of tweezers. Upon extraction, the hexane is allowed to evaporate until the grid is dry. Two different drying techniques were used: natural evaporation and hot-plate assisted evaporation. For natural evaporation, the grid was allowed to sit in ambient conditions until dry whereas in hot-plated assisted evaporation, the TEM Grid was suspended a half-inch over the hot-plate surface via a pair of tweezers and allowed to dry with the hot-plate set at 50 C. Both of these techniques yielded inconsistent results on a grid-to-grid basis. Dispersion of the nanoparticles was relatively non-uniform throughout the mesh of the grid and results displayed a high level of agglomeration of nanoparticles in meshes where material was present.

In the vacuum drying method, an eye-dropper was utilized to place a drop of colloidal cobalt solution onto the TEM grid. The grid was then placed in vacuum chamber for drying. This method was very ineffective because the strength of the vacuum overwhelmed the grid and solution. In many cases the grid was damaged and in other cases the grids which maintained form were found to have little to no material deposited on them.

The drop-method, suggested by Kurt Langworthy from the Electron Microscope Facility at the University of Oregon, was utilized in an effort to control the exposure of the TEM grid to the colloidal solution with the goal to maximize dispersion and minimize agglomeration. The TEM grid was suspended a half-inch over a hot-plate set at 50 C. A glass pipette was utilized to add small drops of colloidal cobalt solution, one at a time, to the TEM grid, allowing sufficient time for drying in between additions. This technique yielded better results relative to the dip-method, however, agglomeration still served as a major issue.

The spray-method has been the most utilized technique for TEM analysis. Dr. Andrew M. Minor from the National Center of Electron Microscopy at Lawrence Berkeley National Laboratory suggested utilizing a nebulizer which creates an atomized mist from colloidal solution. In this technique the TEM grid is sprayed with colloidal cobalt suspension using the nebulizer, shown in Figure 14.

Figure 14. Nebulizer

Ten milliliters of colloidal solution are placed into the nebulizer. After attaching the bulb assembly, the nebulizer is utilized to horizontally spray an ultra-fine mist of colloidal solution onto a TEM grid, which is held in front of its nozzle with a pair of tweezers. The TEM grid is allowed approximately 5 minutes to dry off excess solvent and then analyzed using the Zeiss EM109 electron microscope. Results via the spray-method provided consistent results of well-dispersed nanoparticles in discrete hexagonal networks throughout the TEM grid meshes. The TEM sample preparation sequence is summarized in Figure 15.

Figure 15. TEM sample preparation sequence.

TEM images were captured via camera on high-resolution film. Standard dark-room techniques were utilized to develop the negatives and prints. The prints were then scanned into JPG image files using a Canon 3200dpi scanner. UTHSCSA Image Tool 3 imaging software, developed at the University of Texas Health Science Center at San Antonio, was utilized to perform particle sizing analysis.

3.8 Vibrating Sample Magnetometer Sample Preparation and Analysis

A vibrating sample magnetometer was utilized to capture the magnetic response of a sample under a varying magnetic field. The VSM utilized in this research is displayed in Figure 16.

Figure 16. Vibrating sample magnetometer.

The VSM is attached to a control module, shown in Figure 17, which extracts measurements from the VSM and relays it to a computer.

Figure 17. VSM control module.

XRD samples are used directly for VSM analysis. The preparation technique is outlined in Figure 13. Once the samples are ready, they are mounted onto the VSM sample holder via double-sided tape. In this research analysis was conducted at room temperature.

CHAPTER FOUR: RESULTS

4.1 XRD Pattern Analysis

Figures 18-21 display the XRD scan results for cobalt nanoparticles synthesized using trioctylphosphine (t-octyl) at a high surfactant-to-reagent (HSR) molar ratio, t-octyl at low surfactant-to-reagent (LSR) molar ratio, tributylphosphine (t-butyl) at a HSR molar ratio, and t-butyl at a LSR molar ratio, respectively.

Figure 18. XRD scan result of t-octyl HSR molar ratio synthesized cobalt nanoparticles (Alza Corp.).

Figure 19. XRD scan results of t-octyl LSR molar ratio synthesized cobalt nanoparticles (Alza Corp.).

Figure 20. XRD scan result of t-butyl HSR molar ratio synthesized cobalt nanoparticles (Alza Corp.).

All four scans show four peaks near the same relative angles. The t-butyl LSR scan shows a peak at $2\theta = 41.727$, at relatively low intensity. Table 5 summarizes the major peaks and relative intensities seen in all four sample scans.

Table 5. XRD major peaks and relative intensities for cobalt nanoparticles synthesized using trioctylphosphine (t-octyl) at a high surfactant-to-reagent (HSR) molar ratio, t-octyl at low surfactant-to-reagent (LSR) molar ratio, tributylphosphine (t-butyl) at a HSR molar ratio, and t-butyl at a LSR molar ratio.

t-octyl HSR		t-octyl LSR		t-butyl HSR		t-butyl LSR	
2θ	Rel. Int. (%)	2θ	Rel. Int. (%)	2θ	Rel. Int. (%)	2θ	Rel. Int. (%)
44.5943	100.00	44.5195	100.00	44.6469	100.00	41.727	6.30
46.1929	23.88	45.6878	16.42	46.2646	25.25	44.504	100.00
47.1700	32.60	47.1106	29.44	47.1535	32.87	46.217	29.30
49.6428	15.50	49.5219	16.23	49.6164	17.84	47.013	34.90
						49.495	16.10

Re-arranging and using Bragg's Law in Equation 4, the observed d-spacing was calculated for each of these peaks. Table 6 displays the d-spacings for the largest diffraction peaks for all four sets of syntheses conditions.

$$d = \frac{\lambda}{2 \sin \theta} \quad \text{Equation 4}$$

Table 6. Observed d-spacings for cobalt nanoparticles at largest diffraction angle.

Condition	Peak (2 θ)	d-spacing (Å)
t-octyl HSR	49.6248	1.8350
t-octyl LSR	49.5219	1.8392
t-butyl HSR	49.6164	1.8359
t-butyl LSR	49.4950	1.8401

The results in Table 6 show d-spacing values very similar to each other, which is as expected since the major peak angles are very similar.

Using Equation 5 with the assumption a cubic structure, the observed d-spacings, and the lattice parameter of cobalt, each diffraction peak in Table 4 was indexed to a crystal plane. Sun et al. have reported a lattice parameter of 6.30 Å for the ϵ -cobalt structure [16]. Table 7 displays plane indexing results based on matching $\sin^2(\theta)$ to $(\lambda^2/4a^2)(h^2+k^2+l^2)$ in Equation 5.

$$\frac{1}{d^2} = \frac{4 \sin^2 \theta}{\lambda^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad \text{Equation 5}$$

Table 7. Plane indexing results for cobalt nanoparticles.

t-octyl HSR		t-octyl LSR		t-butyl HSR		t-butyl LSR		Indexed
$\sin^2(\theta)$	Match	$\sin^2(\theta)$	Match	$\sin^2(\theta)$	Match	$\sin^2(\theta)$	Match	Plane
						0.1268	0.1266	111
0.1440	0.1440	0.1435	0.1435	0.1443	0.1442	0.1434	0.1437	442
0.1539	0.1539	0.1507	0.1507	0.1543	0.1543	0.1540	0.1540	620
0.1601	0.1602	0.1597	0.1597	0.1600	0.1602	0.1591	0.1592	620
0.1761	0.1760	0.1754	0.1754	0.1760	0.1760	0.1752	0.1751	311

Table 7 shows that the peaks in Figure 18-21 are associated with the (442), (620), (620), and (311) crystal planes. This simplifies to the primitive planes: (221), (310), (310), and (311) which is associated with the ϵ -cobalt crystal structure [13,16,30]. The scan in Figure 21, shows a peak at $2\theta = 41.727$ which is associated with the (111) plane.

For the ϵ -cobalt crystal structure, the (221) plane is known to show the greatest level of diffraction intensity [13,16]. Table 8 summarizes the major peaks, relative intensities and indexed planes for all four scans.

Table 8. Major peaks, scan intensities, and indexed planes for cobalt nanoparticles.

t-octyl HSR		t-octyl LSR		t-butyl HSR		t-butyl LSR		Planes
2θ	Rel. Int. (%)	2θ	Rel. Int. (%)	2θ	Rel. Int. (%)	2θ	Rel. Int. (%)	hkl
						41.7270	6.30	111
44.5943	100.00	44.5195	100.00	44.6469	100.00	44.5040	100.00	442
46.1929	23.88	45.6878	16.42	46.2646	25.25	46.2170	29.30	620
47.1700	32.60	47.1106	29.44	47.1535	32.87	47.0130	34.90	620
49.6428	15.50	49.5219	16.23	49.6164	17.84	49.4950	16.10	311

The results in Table 8 display an excellent match with 100% relative intensity on the (442) plane for all samples. The (221) and (310) planes are not seen in the XRD pattern due to extinction. ϵ -cobalt is a form of the β -manganese crystal structure which follows a fcc cubic structure, however, with atoms at unequal distances from each other [5]. For calculation purposes a typical fcc structure is assumed, hence atomic locations

are known to be (0,0,0), ($\frac{1}{2}$, $\frac{1}{2}$, 0), ($\frac{1}{2}$, 0, $\frac{1}{2}$), (0, $\frac{1}{2}$, $\frac{1}{2}$). Using Equation 6, the structure factor can be calculated which provides information on extinction of planes.

$$F = f_{Co} + f_{Co} \exp[2\pi i(0.5h + 0.5k + 0l)] + f_{Co} \exp[2\pi i(0h + 0.5k + 0.5l)] + f_{Co} \exp[2\pi i(0.5h + 0k + 0.5l)] \quad \text{Equation 6}$$

In Equation 6, when the integer within the exponent is odd or even, the exponent has a value of -1 or +1, respectively. The value of the atomic scattering factor, f_{Co} , is determined using tabulated data [19]. Plotting tabulated values of f_{Co} versus diffraction angle, the relationship in Equation 7 is established for the atomic scattering factor of cobalt, f_{Co} .

$$f_{Co} = 25.35e^{-1.35 \frac{\sin \theta}{\lambda}} \quad \text{Equation 7}$$

Tables 9-12, display the calculated structure factor, F, indicating planes which diffract for trioctylphosphine and tributylphosphine synthesized nanoparticles, respectively.

Table 9. Structure factor, F, for t-octyl HSR cobalt nanoparticles.

t-octyl HSR					Plane
2 θ	$\sin(\theta) / \lambda$	f(Co)	F(Co)	Int.(rel)	(hkl)
44.5943	0.2463	18.1798	72.7190	100.00%	442
46.1929	0.2546	17.9759	71.9035	23.88%	620
47.1700	0.2597	17.8530	71.4119	32.60%	620
49.6248	0.2724	17.5499	70.1996	15.50%	311

Table 10. Structure factor, F, for t-octyl LSR cobalt nanoparticles.

t-octyl LSR					Plane
2 θ	$\sin(\theta) / \lambda$	f(Co)	F(Co)	Int.(rel)	(hkl)
44.5195	0.2459	18.1894	72.7575	100.00%	442
45.6878	0.2520	18.0399	72.1597	16.42%	620
47.1106	0.2594	17.8604	71.4416	29.44%	620
49.5219	0.2719	17.5624	70.2498	16.23%	311

Table 11. Structure factor, F, for t-butyl HSR cobalt nanoparticles.

t-butyl HSR					Plane
2θ	$\sin(\theta) / \lambda$	$f(\text{Co})$	$F(\text{Co})$	Int.(rel)	(hkl)
					111
44.6469	0.2465	18.1730	72.6920	100.00%	442
46.2646	0.2550	17.9668	71.8673	25.25%	620
47.1535	0.2596	17.8550	71.4202	32.87%	620
49.6164	0.2723	17.5509	70.2037	17.84%	311

Table 12. Structure factor, F, for t-butyl LSR cobalt nanoparticles.

t-butyl LSR					Plane
2θ	$\sin(\theta) / \lambda$	$f(\text{Co})$	$F(\text{Co})$	Int.(rel)	(hkl)
41.7270	0.2312	18.5542	74.2169	6.30%	111
44.5040	0.2458	18.1914	72.7655	100.00%	442
46.2170	0.2548	17.9728	71.8913	29.30%	620
47.0130	0.2589	17.8726	71.4906	34.90%	620
49.4950	0.2717	17.5657	70.2629	16.10%	311

From Sun et al., the lattice parameter for the ϵ -cobalt structure is reported as 6.30 Å [16]. To confirm Equation 5 is utilized to calculate the observed lattice parameter for the indexed planes for ϵ -cobalt. Table 13 displays the observed lattice parameter for each indexed plane for each synthesis condition. At the largest 2θ value, the results show a lattice parameter of 6.2983, 6.2995, 6.2993, and 6.2974 Å for t-octyl HSR, t-octyl LSR, t-butyl HSR, t-butyl LSR synthesis conditions, respectively. The calculated lattice parameters at the largest diffraction peaks are within 0.05% of the value reported by Sun et al.

Table 13. Observed lattice parameter for indexed planes ϵ -cobalt nanoparticles.

Plane (hkl)	t-octyl HSR (Å)	t-octyl LSR (Å)	t-butyl HSR (Å)	t-butyl LSR (Å)
111				6.2946
442 - 221	6.3003	6.3008	6.2992	6.3067
620 - 310	6.2996	6.3002	6.2997	6.2997
620 - 310	6.3013	6.2995	6.3033	6.3027
311	6.2983	6.2995	6.2993	6.2974

The lattice parameters calculated in Table 13, however, do not account for systematic error associated with the analysis. The systematic error results because the x-ray focused beam is not in the plane of the sample; hence, the entirety of the sample is not at the focal point of the beam. This systematic error is larger at low angles and should be accounted for in order to have a more precise lattice parameter value [19]. Assuming that the largest source of error in the measurement is the displacement of the sample from the diffractometer axis, an extrapolation of the lattice parameter can be made from Equation 8. This corrective method only applies to Bragg-Brentano geometry [19]. Hence, it is not utilized for t-butyl LSR which was scanned using parallel beam alignment.

$$a = a_o + a_o k \frac{\cos^2 \theta}{\sin \theta} \quad \text{Equation 8}$$

In Equation 8, a is the observed lattice parameter from indexed planes listed in Table 13, θ is the diffraction angle, and a_o is the calculated lattice parameter. A plot of a vs. $(\cos^2 \theta)/(\sin \theta)$ for t-octyl HSR, t-octyl LSR, and t-butyl HSR molar ratio synthesis conditions is displayed in Figure 22.

Figure 22. Corrected lattice parameter vs. diffraction angle for t-octyl HSR, t-octyl LSR, and t-butyl HSR molar ratio synthesized ϵ -cobalt nanoparticles. $R^2=0.90, 0.92, 0.81$, respectively.

Linear fitted lines to the data in Figure 22 yield an extrapolation to the y-intercept which is a corrected lattice parameter value. Table 14 summarizes the corrected lattice parameter values for all synthesis conditions. The results in Table 14 indicate that the corrected lattice parameters are within 0.25% of the value reported by Sun et al.

Table 14. Corrected lattice parameter for all cobalt nanoparticle syntheses conditions.

Condition	Corrected Lattice Parameter, a (Å)
t-octyl HSR	6.2860
t-octyl LSR	6.2900
t-butyl HSR	6.3030
t-butyl LSR	N/A

The sample utilized in this analysis is assumed to be a randomly oriented powder. In order to evaluate the nature of randomization, intensity is calculated using Equation 9 and compared to the results of the scan.

$$I_{hkl} = |F|^2 p L_p e^{-2M} \quad \text{Equation 9}$$

In Equation 9, F is the structure factor, p is the multiplicity factor, L_p is the Lorenz Polarization factor, and M is the temperature factor. The structure factor results for all syntheses conditions are provided in Tables 9-12. The multiplicity factor is acquired from reference tables and the temperature factor, M, is determined by Equation 10.

$$M = \left[\frac{11500T}{A\Theta} \right] \left[\phi(x) + \frac{x}{4} \right] \left(\frac{\sin \theta}{\lambda} \right)^2 \quad \text{Equation 10}$$

In Equation 10, T is temperature of the sample taken to be 298K, A is the atomic weight, 58.933, Θ is the Debeye temperature which is 385K for cobalt, $\phi(x)$ is acquired from reference tables [19], x is defined as T/ Θ , θ is the diffraction angle, and λ is 1.5406 Å.

Table 15 displays the calculated intensity results along with the results from the scan. The calculated intensity results are normalized to the highest intensity plane (422/221) to get relative intensity. The calculated results and scan results indicate that the (442) is the strongest intensity plane. However, there is a significant difference in relative intensities when comparing the calculated and observed intensities for the (620) and (311) planes. The calculated intensity indicates a strong diffraction intensity is expected, however, the observed relative intensities indicate a sharp drop-off from the

(442) to the (620) and (311) planes. This result is consistent across all synthesis conditions.

Table 15. Calculated vs. scan relative intensity results for cobalt nanoparticles.

Planes (hkl)	t-octyl HSR		t-octyl LSR		t-butyl HSR		t-butyl LSR	
	I/I(442)	I/Io	I/I(442)	I/Io	I/I(442)	I/Io	I/I(442)	I/Io
	Calc. (%)	Obs. (%)	Calc. (%)	Obs. (%)	Calc. (%)	Obs. (%)	Calc. (%)	Obs. (%)
111							40.07	6.30
442	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
620	90.29	23.88	92.78	16.42	90.19	25.25	89.63	29.30
620	84.94	32.60	84.84	29.44	85.31	32.87	85.27	34.90
311	73.14	15.50	73.24	16.23	73.43	17.84	73.28	16.10

4.2 Particle Imaging, Size, and Size Distribution Analysis

After attempting many different techniques, the best TEM results were acquired by using samples which were prepared by the spray-method. In this method, isolated solutions of cobalt nanoparticles were placed in a nebulizer. The nebulizer was utilized to create a fine mist which was sprayed onto a TEM grid. Figure 23 displays a TEM image of t-octyl HSR synthesized cobalt nanoparticles at 400,000 times magnification.

Figure 23. TEM image of t-octyl HSR molar ratio synthesis cobalt nanoparticles at 400Kx magnification, Bar = 10nm.

Figure 24 displays a TEM image of t-octyl LSR synthesized cobalt nanoparticles at 140,000 times magnification.

Figure 24. TEM image of t-octyl LSR molar ratio synthesis cobalt nanoparticles at 140Kx magnification, Bar = 10nm.

Figure 25 displays a TEM image of t-butyl HSR synthesized cobalt nanoparticles at 400,000 times magnification.

Figure 25. TEM image of t-butyl HSR molar ratio synthesis cobalt nanoparticles at 400Kx magnification, Bar = 25nm.

Figure 26 displays a TEM image of t-butyl HSR synthesized cobalt nanoparticles at 400,000 times magnification.

Figure 26. TEM image of t-butyl LSR molar ratio synthesis cobalt nanoparticles at 400Kx magnification, Bar = 50nm.

Images were captured in sufficient quantity to be able to size at a minimum 1000 particles for each synthesis condition. UTHSCSA Image Tool 3 imaging software, developed at the University of Texas Health Science Center at San Antonio, was utilized

to perform particle sizing analysis. Figure 27 displays a boxplot of size versus surfactant utilized for cobalt nanoparticle synthesis.

Figure 27. Boxplot of size versus surfactant used for cobalt nanoparticle synthesis.

Figure 27 displays utilizing trioctylphosphine versus tributylphosphine yields a smaller average nanoparticle size. Figure 28 displays a histogram of cobalt nanoparticle size versus surfactant utilized. In Figure 28, the solid line indicates trioctylphosphine and the dashed line indicates tributylphosphine.

Figure 28. Lognormal histogram of cobalt nanoparticle size versus surfactant.

The results in Figures 27 and 28 show that utilizing trioctylphosphine as a surfactant yields an average cobalt nanoparticle size of 8.05 ± 1.59 nm, whereas tributylphosphine yields 13.65 ± 1.61 nm. This data set is further divided into a boxplot of size versus t-octyl HSR, t-octyl LSR, t-butyl HSR, and t-butyl LSR synthesis conditions, displayed in Figure 29.

Figure 29. Boxplot of cobalt nanoparticle size versus synthesis condition.

Figure 29 displays that using a higher molar ratio of surfactant-to-reagent yields a smaller average nanoparticle size. Figure 30 displays a histogram of size versus t-octyl HSR, t-octyl LSR, t-butyl HSR, and t-butyl LSR synthesis conditions.

Figure 30. Lognormal histogram of cobalt nanoparticle size versus surfactant and synthesis condition.

The resultant nanoparticle sizes in Figures 29 and 30 are summarized in Table 16.

Table 16. Nanoparticle size for t-octyl HSR, t-octyl LSR, t-butyl HSR, and t-butyl LSR molar ratio syntheses conditions.

Condition	Size (nm)	Population
t-octyl HSR	6.87 ± 0.89	1009
t-octyl LSR	9.22 ± 1.24	1009
t-butyl HSR	12.47 ± 0.88	1009
t-butyl LSR	14.84 ± 1.26	1009

4.3 VSM Analysis

VSM analysis was conducted in the Solid State Physics Laboratory, SCI250, at San Jose State University. Samples utilized for XRD analysis were used directly for VSM analysis. The samples are approximately 3-5mg in weight deposited on a 5x5mm silicon substrate. For magnetic measurements, a field range of $-10,000$ to $+10,000$ Oe was

applied. Figure 31 displays moment versus field overlay for cobalt nanoparticles at all syntheses conditions.

Figure 31. Normalized magnetization versus applied field for t-octyl HSR (solid black), t-octyl LSR (dashed black), t-butyl HSR (solid gray), and t-octyl LSR (dashed gray) synthesis conditions.

For all synthesis conditions, cobalt nanoparticles display ferromagnetic behavior at room temperature.

The coercive fields for each synthesis condition were found to be between 390-500 Oe. Smaller particles synthesized using trioctylphosphine displayed a lower coercivity compared to larger particles synthesized using tributylphosphine. Table 17 summarizes the coercivity for all synthesis conditions.

Table 17. Coercive fields for cobalt nanoparticles.

Condition	Mean Particle Size (nm)	Coercivity (Oe)
t-octyl HSR	6.87 ± 0.89	393.4
t-octyl LSR	9.22 ± 1.22	397.6
t-butyl HSR	12.47 ± 0.88	397.3
t-butyl LSR	14.84 ± 1.26	493.6

CHAPTER FIVE: DISCUSSION

5.1 XRD Pattern Analysis

The XRD pattern analysis results in Table 6 show that the observed d-spacing is very similar for all synthesis conditions in this experiment. Table 7 shows that the plane indexing for each synthesis condition matches with the (442) plane displaying the strongest diffraction intensity with the (620) and (311) planes following. The t-butyl LSR condition does show diffraction at low intensity at the (111) plane. This yields two conclusions: first, all synthesis conditions yield the same crystal structure and second, the crystal structure is not the hexagonal close packed structure found at ambient conditions or the face-centered cubic (fcc) structure observed at temperatures above 722 K, in bulk cobalt. The pattern results for all synthesized samples show the (442), (620), and (311) displaying the strongest intensity. These planes are indicative of a meta-stable structure, ϵ -cobalt, which is a form of the β -manganese crystal structure. The (111) plane seen in the t-butyl LSR sample is an occurrence due to two possible reasons: low energy stacking faults yielding diffraction at (111) and possible oxidation. Solution based synthesis is not thermodynamically controlled and hence low energy stacking faults are a probable phenomena seen in nanoparticles [16]. The other scenario is the possibility of oxidation: cobalt oxide has a NaCl crystal structure which would diffract at (111) planes with 2θ values very close to the observed scan value. Since the intensity of the peak is low relative to the others either could be a viable scenario, however, the sample does continue to show strongest diffraction intensity in the (442), (620), and (311) planes, which follows the ϵ -cobalt symmetry. This crystal structure is a complex form of the primitive

cubic cell with 20 atoms within at unequal separation distances [16]. The primitive planes which are characteristic of the ϵ -cobalt structure are (221), (310), and (311). Atomic scattering factor calculations based on Equation 6, which are summarized in Tables 9-12 show that the first two planes, (221) and (310) are not seen in the diffraction pattern due to systematic extinction. The scan results for each synthesis condition also show that there are two peaks, both index to the (620) plane. This splitting could be due to $\text{Cu}_{K\alpha 1}$ and $\text{Cu}_{K\alpha 2}$ radiation; however, this is largely seen at higher wavelengths. A more probable cause is low energy stacking faults in the crystal. The hexagonal closed packed (hcp) structure of cobalt has a diffraction peak which lies approximately $2\theta=46.5$ degrees which is very close to the first peak indexed at (620) in all synthesis conditions.

The lattice parameter reported by Sun et al. is 6.30 Å [16]. In this study, at highest diffraction angle, the results show a lattice parameter of 6.2983, 6.2995, 6.2993, and 6.2974 Å for t-octyl HSR, t-octyl LSR, t-butyl HSR, t-butyl LSR synthesis conditions, respectively. These values are within 0.05% of the reported value by Sun et al. The observed lattice parameter does not take into account systematic error which can be corrected for samples characterized using Bragg-Brentano geometry. The results from this calculation yield a corrected lattice parameter of 6.286, 6.290, and 6.303, for t-octyl HSR, t-octyl LSR, t-butyl HSR synthesis conditions, respectively. The scan of t-butyl LSR was done using parallel beam geometry for which the corrected lattice parameter analysis is invalid. The corrected lattice parameter values are within 0.25% of that reported by Sun et al.

In Table 15, the calculated intensity results are shown versus the actual intensity results from each synthesis condition scan. The results in Table 15 show that calculated results and scan results indicate that the (442) is the strongest intensity plane across all syntheses conditions. There is a significant difference in relative intensities when comparing the calculated and observed intensities for the (620) and (311) planes. The calculated intensity indicate a strong diffraction intensity is expected, however, the observed relative intensities indicate a sharp drop-off from the (442) to the (620) and (311) planes. This result is consistent across all synthesis conditions. This result is indicative that the samples in all syntheses conditions are not randomized powders, rather, they have a preference in orientation which is consistent across all conditions and shows alignment to the strongest diffracting plane, (442).

5.2 TEM, Sizing and Size Distribution Analysis

In Figures 23-26 TEM scans for each synthesis condition display cobalt nanoparticles in discrete hexagonal networks across the TEM grid sections. This hexagonal network is formed on a consistent basis and the scans display particles within the network are separated by an average range of 2-5 nm. The density of the network is largely dictated by the amount of polar to non-polar solvent washes performed. The number of washes yields a purified dilute solution. Figures 23, 25, and 26 are characteristic of solutions washed 3-5 times. Figure 24 represents a solution which underwent a series of 7 washes yielding a less dense string network. This is indicative that 3-5 wash cycles yields a dense network of nanoparticles and further wash cycles yield nanoparticle loss yielding less dense networks.

Sizing results in Figure 27 and 28 show a boxplot and histogram of t-octyl synthesized versus t-butyl synthesized nanoparticles, respectively. The boxplot and histogram show visual evidence of distinction between the t-butyl and t-octyl synthesized particles. The histogram was plotted using a lognormal fit in order to exploit asymmetry; however, the results in Figure 28 display a Gaussian distribution with mild deviations for both groups of nanoparticles. Figures 29 and 30 display a further breakdown of the overall data to the four synthesis conditions: t-octyl HSR, t-octyl LSR, t-butyl HSR, and t-butyl LSR. The histogram in Figure 30 was also plotted using a lognormal fit to exploit any form of asymmetry; however, again the distributions are Gaussian with mild deviations. To compare the mean particle size among the groups, a two sample t-test assuming unequal variances analysis was conducted. The analysis is based on a two-tail distribution with a 99% confidence level. The results are summarized in Table 18.

Table 18. P(two-tail) two samples assuming unequal variances at 99% confidence matrix for comparing the average size of cobalt nanoparticles.

	t-octyl All	t-octyl HSR	t-octyl LSR	t-butyl HSR	t-butyl LSR	t-butyl All
t-octyl All	-	-	-	< 0.1%	< 0.1%	< 0.1%
t-octyl HSR	-	-	< 0.1%	< 0.1%	< 0.1%	< 0.1%
t-octyl LSR	-	< 0.1%	-	< 0.1%	< 0.1%	< 0.1%
t-butyl HSR	< 0.1%	< 0.1%	< 0.1%	-	< 0.1%	-
t-butyl LSR	< 0.1%	< 0.1%	< 0.1%	< 0.1%	-	-
t-butyl All	< 0.1%	< 0.1%	< 0.1%	-	-	-

Table 18 displays comparisons between all t-test combinations. First combined data for t-octyl is compared to t-butyl synthesis. The results indicate the probability that

the mean particle size is different between t-octyl versus t-butyl based synthesis due to chance is less than 0.1%. Conversely, the probability that the two mean particles sizes are different due to the surfactant utilized is greater than 99%. Similarly comparing t-octyl HSR mean versus t-octyl LSR mean particle size shows that the probability that the two means are different due to the difference in surfactant-to-reagent ratio is greater than 99%. The results in comparing t-butyl HSR and t-butyl LSR synthesis conditions yields the same result. For completeness, the other combinations were analyzed as well and all indicate significant statistical differences.

5.3 VSM Analysis

The overlaid M-H graphs in Figure 31 display open hysteresis loops for all syntheses conditions, indicating ferromagnetic behavior at room temperature. The results in Table 17 show coercivity values between 390-500 Oe indicating that the synthesized cobalt nanoparticles behave as single domain magnets. The coercivity can be seen increasing with nanoparticle size, with smaller t-octyl synthesized particles displaying lower coercive field compared to larger t-butyl synthesized particles.

CHAPTER SIX: SUMMARY AND CONCLUSION

6.1 Summary

In this study, cobalt nanoparticles were synthesized via high temperature thermal oxidation and reduction of cobalt (II) chloride utilizing two surfactants; tributylphosphine and trioctylphosphine at 2:1 and 4:1 surfactant-to-reagent molar ratios. An x-ray diffractometer, transmission electron microscope, and a vibrating sample magnetometer were used to analyze the synthesis product for elemental identification and crystal structure, particle size and morphology, and magnetic behavior, respectively.

The XRD results of this study indicate that all synthesis conditions yield cobalt as the final product. Crystallographic analysis indicates that all syntheses conditions yield a meta-stable structure known as ϵ -cobalt. For t-octyl HSR, t-octyl LSR, and t-butyl HSR syntheses conditions, the corrected lattice parameters for ϵ -cobalt were 6.2860, 6.2900, and 6.3030 Å, respectively. The t-butyl LSR sample was scanned using parallel beam geometry and had an observed lattice parameter of 6.2974 Å. These lattice parameter values were found to be within 0.25% of the reported value by Sun et al.

TEM results of this study display the formation of spherical cobalt nanoparticles with a dense metallic core surrounded by an organic shell for all syntheses conditions. A TEM sample preparation method was developed which utilizes a series of polar and non-polar solvent washes to isolate the product and a nebulizer to apply the nanoparticles to a TEM grid. The results show the formation of discrete hexagonal networks across TEM grid samples with an average separation distance of 2-5 nm between nanoparticles.

Results also show that increasing the number of washes yields a less dense string-like network of nanoparticles.

Particle size analysis was conducted utilizing ImageTool software developed by the University of Texas Health Science Center at San Antonio. The results show that trioctylphosphine based synthesis yields an average particle size of 8.05 ± 1.59 nm and tributylphosphine based synthesis yields 13.65 ± 1.61 nm. Further partitioning the results into the four synthesis condition found an average size of 6.87 ± 0.89 , 9.22 ± 1.24 , 12.47 ± 0.88 , 14.84 ± 1.26 nm for t-octyl HSR, t-octyl LSR, t-butyl HSR, and t-butyl LSR condition, respectively. Statistical analysis was performed to compare the means of each synthesis condition and the results indicate that each mean is statistically significant.

Magnetic analysis was done at ambient temperature utilizing a vibrating sample magnetometer, applying a field ranging from -10,000 to 10,000 Oe. For all syntheses conditions, the results display open hysteresis loops indicative of ferromagnetic behavior at room temperature. Coercivity was calculated to be between 390-500 Oe for all syntheses conditions, indicative that the cobalt nanoparticles behave as single domain magnets with smaller trioctylphosphine synthesized nanoparticles displaying lower coercivity relative to larger nanoparticles synthesized by tributylphosphine.

6.2 Conclusions

All the objectives of this research were successfully met. Magnetic cobalt nanoparticles were successfully synthesized via thermal oxidation-reduction of cobalt (II) chloride. X-ray diffraction characterization displayed the formation of an ϵ -cobalt

structure for all syntheses conditions. Analysis found a lattice parameter within 0.25% of the literature reported 6.30 Å.

By utilizing two surfactants with differing size alkyl side chains, it was demonstrated that mean nanoparticle size can be controlled, with the bulkier trioctylphosphine yielding smaller average nanoparticles. It was further demonstrated that varying the surfactant-to-reagent molar ratio also serves to control mean particle size, with higher surfactant-to-reagent molar ratio yielding small particles. Magnetic analysis displayed open hysteresis loops for all syntheses conditions, indicating room-temperature ferromagnetic behavior. Further analysis found that coercivity ranged from 390 to 500 Oe, with small nanoparticles displaying lower coercive field relative to larger particles.

6.3 Future Work

The development of cobalt nanoparticles remains in its early phases. Synthesis techniques and characterization methods have been proven. There are many objectives to follow up in research in order to make cobalt nanoparticles a viable industrial product.

Stability is one of the foremost concerns to address. Current research has not shown any demonstration of long-term stability of synthesized nanoparticles. In order to be viable for marketable products, these nanoparticles have to be proven to be stable for extended periods of time. Particle size, distribution, morphology, and agglomeration are key parameters to monitor in order to understand and attack concerns of stability.

Disposal methods are a follow-up concerns. Magnetic nanoparticles such as cobalt are toxic and adequate and appropriate methods for neutralization and disposal are necessary in order to make manufacturing environmentally feasible. For industrial

applications, hazardous waste containment and disaster handling methods are crucial criteria.

Scale-up is the utmost of facets to address. Current research has demonstrated synthesis and product yields on a bench-scale. Future research must analyze the effects of scale and how particle size, size control, morphology behave with increases in production scale. Current research displays bench-scale synthesis yield of less than 20% with most experimental studies yielding on the order of 1-5%. In order to be viable for manufacturing yield has to achieve a minimum of 80%.

The field of nanotechnology products is immense; however, without proper development of these technologies, there will be no fruition.

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