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The Synthesis and Characterization of Iron Nanoparticles

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THE SYNTHESIS AND CHARACTERIZATION OF IRON NANOPARTICLES

By

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B.A., Wheaton College, 2012

THESIS

Submitted to the University of New Hampshire
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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF IRON NANOPARTICLES

By

Tyler Bennett

University of New Hampshire, September 2015

Nanoparticle synthesis has garnered attention for technological applications for catalysts, industrial processing, and medical applications. The size ranges for these is in the particles nanostructural domain. Pure iron nanoparticles have been of particular interest for their reactivity and relative biological inertness. Applications include cancer treatment and carrying medicine to a relevant site. Unfortunately, because of their reactivity, pure iron nanoparticles have been difficult to study. This is because of their accelerated tendency to form oxides in air, due to the increased surface area to volume ratio. Using synthesis processes with polyphenols or long chain amines, air stable iron nanoparticles have been produced with a diameter size range of ~2 to about ~10 nm, but apparently have transformed due to internal pressure and crystallographic defects to the FCC phase. The FCC crystals have been seen to form icosahedral and decahedral shapes. This size is within the range for use as a catalyst for the growth of both carbon nanotubes and boron nitride nanotubes as well for biomedical applications. The advantages of these kinds of catalysts are that nanotube growth can be for the first time separated from the catalyst formation. Additionally, the catalyst size can be preselected for a certain size nanotube to grow. In summary: (1) we found the size distributions of nanoparticles for various synthesis processes, (2) we discovered the right size range for growth of nanotubes from the iron nanoparticles, (3) the nanoparticles are under a very high internal pressure, (4) the nanoparticles are in the FCC phase, (5) they appear to be in icosahedral and decahedral structures, (6) they undergo room temperature twinning, (7) the FCC crystals are distorted due to carbon in octahedral sites, (8) the iron
nanoparticles are stable in air, (9) adding small amounts of copper make the iron nanoparticles smaller
Chapter 1: Introduction

Among the most promising applications in nanotechnology include the use of nanoparticles both as nanotube catalysts and in biomedical applications. Nanotubes themselves are an important new kind of material and have applications for shielding electromagnetic interference, shielding electrostatic discharge, very lightweight cables, solar cells, body armor, semiconductor devices as well as many other kinds of industrial commodities. For example, nanoparticles can be used as catalysts for: (1) growing carbon nanotubes (CNTs), (2) catalysts for the Fisher Trope Process, where carbon monoxide is turned into hydrocarbons, (3) a method for drug attachment and (4) delivering drugs to the body where magnetic fields can assist particle motion and insure accurate placement and be used to cause local heating, and finally as environmentally friendly, (5) temperature specific solders. This study focuses on the very reactive metallic iron nanoparticles used for catalysts for boron nitride nanotube synthesis (BNNT) and potentially for carbon nanotube synthesis.

In order for nanoparticles to be most useful, they have to be close to mono-modal in diameter distribution. However, because of the small size of the nanoparticles, they are under an immense amount of internal pressure. This pressure also effects their crystal structure. Pressure in turn is related to particle size, through the Young-Laplace Equation, \( \Delta P = 2\gamma/r \) where the smaller the particle radius “r” the higher the internal pressure, “\( \gamma \)” is the surface energy. Synthesis techniques control the particle size distribution and therefore the internal pressure and phase present. On the nanoscale characterization, handling and surface purity are particularly important processes as the surface is sensitive to contamination. This is especially true for iron because of its tendency to form an oxide in air that is enhanced by the small particle radius, since there is an increased surface area for the smaller particles, allowing for oxygen to bond more readily.
In this work we study and investigate those processing conditions required to fabricate and control sub-10nm diameter size iron nanoparticles, with narrow size distributions. We investigate the structure of the nanoparticles using x-ray diffraction and TEM images. Finally, we use these nanoparticles to catalyze the synthesis of boron nitride and CNT continuous yarn. This latter use of nano-structural iron helps eliminate the serious existing problem of simultaneously producing growth and in situ particle synthesis, which today is common practice. It also allows predetermining the nanotube size prior to the growth process though selection of the particle size.

1.1 Applications of Nanoparticles

There is a wide range of potential applications for nanoparticles. The biomedical industry has been examining the potential of different nanoparticles bounded with medication to be moved to a targeted area. In combination with cancer drugs, nanoparticles have shown an ability to effectively treat many forms of cancer. For example, gold nanoparticles with an anticancer drug 5-flurouracil attached to the surface, can directly target tumors, by breaking this bond with ultraviolet radiation as it reaches its destination [1]. Even without other compounds attached, nanoparticles still have biomedical applications. Gadolinium-157 nanoparticles readily absorb neutron radiation, emitting gamma rays as a result. When they are coated in gadopentacetic acid, these nanoparticles are easily retainable by cancer cells, where an outside neutron radiation source can impinge upon the particles. This would result in selectively irradiating, illuminating, and eliminating the cancer sites. Silver nanoparticles also have been shown to have antiviral properties, which have shown to help block the reproductive binding of HIV to cells [2]. Some nanoparticles have been attached with dyes to allow for better imaging of areas of the body. For example, titanium oxide nanoparticles coated with a fluorescein amine can be imaged even inside of cells to examine their
interaction with DNA and how they are incorporated into the cells [3]. Additionally, nanoparticles are being examined as a means of tracking the spread of cancer throughout the body and induction heating of these particles is being studied as a means of killing cancer without damaging adjacent tissue [4]. If the nanoparticles were uniform in size, it would allow a more efficient treatment of diseases with lower risk of adverse side effects.

Nanoparticles have applications in nanomanufacturing. One example of this can be seen with the production of nanotubes. Currently, the production of fixed chirality or diameter nanotubes has proven elusive. Because of the nanotubes’ sensitivity of physical and electrical properties on the diameter of the nanotubes, the nanotubes limited for some applications, such as in semi-conductors or as a replacement for copper wiring. By using nanoparticles as a catalyst for nanotubes, one can at least measure the diameter distribution of the catalysts prior to growth. One of the more important properties of the nanotubes is the electronic properties. For carbon nanotubes the bandgap is approximately related to the diameter by:

$$BG = \frac{0.7}{d}$$

where “BG” is the band gap in eV and “d” is the diameter of the nanotubes in nanometers [5]. If the diameter of the tubes were such that the band gap would be extremely small, at say 10nm, the nanotubes could be considered a semi-metal. Unfortunately, with current processes, about a third of the nanotubes produced are semiconducting. If a greater percentage of nanotubes produced had a slightly larger of a diameter it might be easier to reach near copper level conductivity. The consequences of replacing heavy copper based cables with CNT cables, which have about half the weight, are profound for many industries, space, automotive, and aircraft. Additionally, because the current use of catalysts grown in-situ in the reaction chamber, the process of growing the nanotubes would be simplified, as the complex thermal processes for making these nanoparticles
will play less of a role. This potentially could lead to larger production of nanotubes with much improved control over size.

Nanoparticles are also being investigated for solder applications in multilayer circuits. Because the melting point decreases as the crystals become smaller, it is possible to make different diameters of solder particles, like those currently made with tin, which melt at different temperatures. The reason for this, is that the melting point depends on particle size at the nanoscale [6,7]. This allows for electronic layering, where different melting point solders can be made so that each successive layer has a lower melting point than the layer beneath it. This would allow electronics to be made in steps where each layer is not affected by the subsequent layer. Additionally, once the lead free solder melts, it will have bulk melting point properties. Another important implication is that the solder will be of uniform composition thereby minimizing galvanic corrosion. This will improve the environmental impact of electronics, by removing lead as a component, as well as the electrical conductivity of the connections [6]. Since tin containing solders can undergo fast-diffusion, and subsequent intermetallic formation, with the copper substrate [8] solder failure often occurs at the embrittled interface due to poor bonding. The approach of using small diameters of more stable solders eliminates this problem, which plagues the automotive and aerospace community [9].

This work will primarily focus on iron and iron alloy nanoparticles. Since iron is a known catalyst for carbon and boron-nitride nanotubes, the catalytic properties of nanoparticles will be tested by the synthesis of nanotubes. While other catalyst nanoparticles, such as cobalt and nickel, have been shown to be better catalysts, they are potentially mutagenic.
1.2 Properties of Iron

Iron is the 26th element in the periodic table, with a molar mass of 55.85g. Its standard melting and boiling point is 1536°C and 2861°C respectively. The Pauline electronegativity is 1.83, which is roughly average with the other transition metals. It has eight oxidation states, from -2 to +6, however, the most preferred are the +2 and +3 states. When it comes into contact with water vapor or damp air, it will readily produce iron oxide. Iron has a resistivity of $9.71 \times 10^{-8} \Omega m$ and its electrical conductivity is $1.03 \times 10^7 S/m$. Thermal conductivity of bulk pure iron is ~80 W/mK. Pure iron is ferromagnetic, with a Curie point at 770 °C. Overall it is very similar to other transition metals, especially cobalt and nickel, and can be seen as a good representation of how other transition metals act in nanoparticle form. A table of how this material compares to others that are used for nanotube synthesis can be seen in Table 1.1.

Table 1.1: A comparison of a few elements used in nanotube synthesis

<table>
<thead>
<tr>
<th>Element</th>
<th>Melting Point (°C)</th>
<th>Boiling Point (°C)</th>
<th>Electrical Conductivity (MS/m)</th>
<th>Common Oxidation states</th>
<th>Electronegativity</th>
<th>Curie Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1536</td>
<td>2861</td>
<td>10.3</td>
<td>+2, +3</td>
<td>1.83</td>
<td>770</td>
</tr>
<tr>
<td>Co</td>
<td>1495</td>
<td>2927</td>
<td>17.2</td>
<td>+2, +3</td>
<td>1.88</td>
<td>1,115</td>
</tr>
<tr>
<td>Ni</td>
<td>1453</td>
<td>2913</td>
<td>14.3</td>
<td>+2, +3, +4</td>
<td>1.91</td>
<td>355</td>
</tr>
<tr>
<td>Mg</td>
<td>639</td>
<td>1091</td>
<td>22.6</td>
<td>+2</td>
<td>1.31</td>
<td>NA</td>
</tr>
<tr>
<td>Rh</td>
<td>1966</td>
<td>3727</td>
<td>21.1</td>
<td>+2, +3, +4</td>
<td>2.28</td>
<td>NA</td>
</tr>
</tbody>
</table>
There are four known allotropes of iron. These can be seen in the temperature-pressure phase diagram in Figure 1.1. Under standard temperature and pressure, iron exists in a body centered cubic phase (BCC) known as \( \alpha \)-iron. As it gains more thermal energy, it becomes more energetically favorable to form a face center cubic (FCC) crystal structure. This is normally referred to as \( \gamma \)-iron, or austenite, and occurs between 912 °C and 1394 °C. \( \gamma \)-iron can hold much more dissolved carbon at 2.04 weight percent (wt%) than \( \alpha \)-iron at 0.021 wt%. It should be noted that FCC iron at these temperatures is paramagnetic rather than ferromagnetic as it is above its Curie point. Increasing pressure up to ~13 GPa, enhances this phase to lower temperatures. Above this 1394°C transition but below the melting point, there exists a second, nonmagnetic BCC phase known as \( \delta \)-iron [11]. Finally, if pressure is greatly increased, the hexagonal closed packed (HCP) crystal structure becomes energetically preferred. This allotrope is known as hexaferrum or \( \varepsilon \)-iron and does not appear at room temperature unless it is put under a pressure of 13 GPa [12].

1.3 Nanoparticle Properties

The properties of nanoparticles are often very different from the properties of the bulk, due to quantum effects. These effects can normally be ignored in a bulk material, but must be taken into account when dealing with the particles. The very large increase in surface area per unit weight
and small radius of curvature can affect the electronic and optical properties of the nanoparticles. The most fundamental change is in the energy levels of the material. In the simplest sense, this can be modeled as a particle in a box. An electron’s wave function has to complete an integral number of wavelengths around the nanoparticles. Because of this only a select number of energies per nanoparticle can be allowed [13]. This shift in energy levels can change the optical-electrical properties of nanoparticles. Because of their discrete energy levels, only specific wavelengths of light that have energies corresponding to differences in electron energy levels, can be absorbed or emitted by the nanoparticles. This can cause a visible change in observed color of the particles. For example, gold nanoparticles gradually become red in color at 30 nm, as they absorb the wavelengths in the green-blue part of the spectrum. As they become larger, the size makes it easier for them to absorb red wavelengths of light, while reflecting the blue, making them appear bluer in color [14].

Nanoparticle iron can also have different allotropes depending on the size of the particle. The smaller the particles are, the more internal pressure the particles will have. The pressure is related to radius as discussed above by the Young-Laplace equation [15]:

$$\Delta P = \frac{2\gamma}{r}$$  \hspace{1cm} (1.2)

where “$\gamma$” is the surface energy of the nanoparticle, “$r$” is the radius, and “$\Delta P$” is the pressure. This equation for iron can be seen in Figure 1.2, which has a $\gamma$ value of 2.2 J/m$^2$. This change in pressure makes it possible for other allotropes of iron to exist at STP. As the nanoparticles form, they actually undergo several transitions to finally end up in BCC form. Simulations have shown that when iron first begins to cluster, they tend to form an icosahedral shape, which is a 20 sided polyhedron with triangular faces. This state only lasts for typically tens of nanoseconds, and typically do not contain more than 50 to 100 atoms. As time goes on, a close packed crystal
structure begins to form, depending on the size of the cluster, it can either be FCC for larger particles, or hexagonal close packed (HCP) for smaller clusters. FCC synthesized nanoparticles have been reported to be as large as 13nm. Above this value, the nanoparticles transition to the most common, BCC allotrope [17].

The electrical properties of nanoparticles below 100nm in diameter deviate dramatically from classical theory. Because of the emergence of discrete energy levels due to the size restrictions of the nanoparticles, ohms law is no longer an applicable model for nanoparticles. Instead, discrete voltage and current levels exist inside the structure. Since the conductivity of the nanoparticles depends on the individual energy bands, only set levels of energy will cause a jump in the conductance. Adding extra energy to the system that does not correspond to a band change, will not increase the current or voltage of the system to the corresponding level. For larger nanoparticles, this effect can be overtaken by thermal energy added to the system. The thermal energy provides the necessary energy to overcome the energy barriers [18].

Figure 1.2: Calculated Internal Pressure of Iron Nanoparticles vs their Diameter compared to the tensile failure strength of different materials [16]
The chemical activity of nanoparticles can be radically different compared with bulk material. As a solid is broken into small pieces, it will have a larger surface area compared with bulk material. An increase in surface area offers more sites for a chemical reaction to take place, increasing the reaction rates. A famous example of this can be seen with titanium, where a solid block is fairly inert to most reactions outside of surface oxidation. However, in nanoparticle form, titanium powder can combust quickly, producing a brilliant white light that is often used in pyrotechnics. Another example is in gold, where it too is inert in bulk form, but tends to be explosive in nanoparticle form. This property has allowed the nanoparticles to be used as a treatment for cancer. The explosion can be caused by excitation with a laser, thus destroying cancer cells with the resulting shock wave [19]. They are also greatly catalytic, and they are being researched for their potential as a fuel cell catalyst [14].

Because of the reactivity of iron nanoparticles with oxygen, the properties of iron nanoparticles have not been as widely studied as their oxide counterparts. This work will aim to address this problem by providing some missing information about iron nanoparticles. The first measurement is size distributions of nanoparticles under various synthesis conditions, for example, temperature, solvent conditions, and concentrations. We focus on conditions needed for (1) monomodal particle sizes, (2) infrared absorption spectra, and (3) x-ray diffraction spectra. The role of alloying is reported to be important [20, 21] so we will add copper to the iron nanoparticles and compare their properties to those of the pure iron nanoparticles.
Chapter 2: Theory

2.1 Models of Nanoparticle Growth

The classical theory of the nucleation and growth of nanoparticles considers small nuclei which form sites where other atoms can attach. These nuclei are often formed chemically, where a metal precursor salt (FeCl$_3$, FeCl$_2$, NiCl$_2$) is reacted with a reducing agent (NaBH$_4$) creating the small metal nuclei. It is possible to have both homogeneous nucleation, where all nanoparticles grow uniformly throughout the solutions and heterogeneous nucleation at sites where there are already nucleation points, such as at the apparatus boundaries, defects, and impurities. In both cases, there is a lower limit to the size of the particles. Below a critical radius ($r_c$), the nanoparticles will be dissolved into the bulk solution, $r_c$ is related to the bulk and surface energies. The equation is as follows [22]:

$$\Delta G = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 \Delta G_v$$

(2.1)

Where “$\Delta G$” is the total free energy of the particle “$r$” is the radius of the particle, “$\gamma$” is the surface energy. “$\Delta G_v$” is the bulk free energy defined as:

$$G_v = -k_B T \frac{\ln(S)}{v}$$

(2.2)

where $k_B$ is Boltzmann’s constant, “$S$” is the ratio of the supersaturation concentration of solute divided by the equilibrium concentration of the solute, “$T$” is the temperature of the system, and “$v$” is the molar volume of the crystal. The critical free energy for stable nuclei formation and the critical radius of this nuclei can be found by taking the derivative of equation 2.1, with respect to $r$, and setting it equal to zero. These are given by the following

$$\Delta G_c = \frac{4}{3} \pi \gamma r_c^2$$

(2.3)

$$r_c = -\frac{2\gamma}{\Delta G_v}$$

(2.4)
where “ΔG_c” is the critical free energy. After their initial nucleation, the growth of the nanoparticles can take many forms. Most classical models assume no interactions between particles. The two limiting growth regimes are; (1) diffusion of the precursor limits the concentration of the atoms in the solution around the nanoparticle, and (2) the surface growth rate of the crystals is slower than the diffusion rate [22]. The equations are:

For the concentration limited case:

\[ \frac{dr}{dt} = \frac{Dv}{r}(C_b - C_r) \]  

(2.5)

And for the surface reactant limited case:

\[ \frac{dr}{dt} = kv(C_b - C_r) \]  

(2.6)

In these equations, “D” is the diffusion coefficient of the atoms in the solution, “k” is the reaction rate, “C_b” is the concentration of the precursor nuclei in the bulk solution, and “C_r” is the maximum solubility of the nuclei in the solution. “v” is the molar volume of the bulk crystal. In the intermediate case, the equation for growth is given by:

\[ \frac{dr}{dt} = \frac{Dv(C_b - C_r)}{r^2 k} \]  

(2.7)

The size distribution of the nanoparticles is partially determined by interactions between nanoparticles. When larger nanoparticles are more energetically favorable, atoms from smaller nanoparticles are transferred to larger nanoparticles, to minimize the total free energy of the system. This process is a form of Ostwald ripening. It is a spontaneous thermodynamic process that decrease the overall surface energy of the system. Larger particles have lower surface energy, due to a smaller surface curvature of the nanoparticles. Additionally, atoms on the inside of the nanoparticles are typically in a lower energy state, in comparison to the surface, as they form into a coherent crystal structure. Smaller, higher energy nanoparticles begin to lose their atoms back
into the solution, eventually particles fall below the critical radius and redissolve completely into the bulk solution [23]. This process somewhat normalizes size distributions. This leaves only the larger nanoparticles which grow from the atoms released during the above process. These growth rates slow down due to the nanoparticles’ lower specific surfaces area and eventually comes to a near stop due to the decrease in atom concentration close to their surfaces. It is possible that particles become sufficiently disperse enough so that smaller particles may not encounter larger particles which would use them to grow. This would occur faster with a more diluted system.

The reverse situation, where smaller particles grow from material taken from larger nanoparticles, can also occur. This is called digestive ripening. This typically occurs when an outside mechanism changes the energy balance, making a certain, smaller sized nanoparticle more desirable. Digestive ripening is the balancing of electrostatic forces of a so-called “digestive capping agent”, with the energy required for the curvature of the nanoparticle [24, 25]. The most common way to do this is by using a long chain amine, thiol, or polyphenol. These chemicals coat the outside of a nanoparticle and due to their electronic structure, tend to repel each other. Therefore, two coated nanoparticles will not be able to merge to form larger particles and reducing their curvature, due to a potential barrier set up by the capping agents [25]. An example of the electronic nature of these particles can be seen in a model of dodecylamine in Figure 2.1. In this figure each segment of black line indicates one carbon-carbon single bond with the appropriate number of hydrogens to fill the four empty places in the electron shell. Since there is a nitrogen atom at one end, there will be a slight polarity of the molecule. This polarity helps orient the molecule such that the more electronegative end (e.g. the nitrogen) will stay closer to the metal while the less electronegative
side will be farther away. Since all of the nanoparticles will have the same coating, the more positive side of the molecules will repeal each other, keeping the nanoparticles from growing much. The effectiveness of these capping agents varies with composition. For example, silver nanoparticles coated in dodecanethiol have an average diameter of 4.5nm, while palladium nanoparticles coated in the same material tend to average closer to 7 nm. The digestive capping agent can be added, pre or post production to reduce nanoparticle sizes. However, in order to be effective, they have to be added at a much greater molar quantity than the base material for the nanoparticles, oftentimes at a 30:1 ratio of capping agent to precursor metal source, is required [24]. While this process requires more capping agents, digestive ripening may lead to a very tight particle size distribution.

2.2 Nanoparticle Size Control

For industrial applications, the control of the size of the nanoparticles is one of the most important considerations. For example, carbon nanotube growth requires a size of the catalyst diameter of between 1/0.7 and 1/0.9 the diameter of the tube [26]. Since the band gap is related to the inverse of this diameter, given by equation 1.1, diameter also affects the electrical properties of the nanotubes. The influence of oxygen on a system can be a huge detriment to most metallic nanoparticles. Oxides readily form on the surface of almost all metals, which can increase the size of these nanoparticles. It can also change the usefulness of the nanoparticles as the surface will have a very different set of properties in comparison with the bulk. The rates of oxidation of nanoparticles can be very high due to thermal effects and high surface area. Reactions with other species can also occur such as reactions with hydroxide, sulfur and nitrogen at high rates. While the oxygen and other impurities can be removed by other means later in the process, it may limit
some applications. For example, in non-forest carbon nanotube growth, where time is a factor for growth, there may not be sufficient time to reduce the iron–oxide nanoparticles to the metallic state, which is required for the catalytic activity.

Not all contaminants increase the size of the nanoparticles. One technique to limit the size of the nanoparticles is to add in a secondary metal to the solution. When the nanoparticle alloys are formed, the impurity metal will diffuse to the primary metal, and often form an alloy [20]. The secondary metal will increase the number of defects in the nanocrystal which may make it more energetically favorable to form new nanoparticles than to continue growing. The downside to this method is that while the particles remain smaller, they can broaden the relative size distribution as well as change the chemical properties of the nanoparticles. Additionally, if there is too much of the secondary metal, the nanoparticles may begin to grow in size [20].

The magnetic and energetic properties of some nanoparticles cause them to tend to cluster together to form macrostructures. These agglomerations are also time dependent, as more nanoparticles are attracted to agglomerations. Given enough time, these nanoparticles may lose their spherical structure and form more crystalline, bulk like structures. As a preventative measure, an ionic surfactant is sometimes added. The surfactant binds to the nanoparticle and repels like coated particles. Although this keeps the nanoparticles from clumping, it causes a similar problem to that which is found with oxidation. The reduction of the surfactant from the surface of the nanoparticles takes time which can limit applications.

Another method of size control is the use of capping agents previously mentioned. The use of long chain carbon molecules has been prevalent in maintaining a near uniform size distribution. These long chain carbon molecules, such as hexadecylamine or octadecylamine, bind to the surface of the iron nanoparticles. These molecules take over sites where other iron atoms could attach to
the particles, reducing their growth, while spacing out the iron cores from each other. In addition, chains will repel each other, which keeps the iron nanoparticle conglomerations small or nonexistent. One study has shown iron-platinum particles as small as 5 ± 2 nm with hexadecylamine and with a small size distribution using dodecylamine with 7 ± 1 nm [27]. While the size distributions would be useful for industrial purposes, the long chains amines will also need to be reduced in order for the nanoparticles to be used.

2.3 Reducing Agents and Solvents for Iron Nanoparticles

In order to obtain iron nanoparticles, a reducing agent needs to be added, to lower the oxidation state of the iron ion. Reducing agents are chemicals that when reacted, give up electrons to the other reactants and usually liberate hydrogen. The reducing agent goes to a higher oxidation state, which is known as being oxidized and maintains the charge balance of the system. The molecule that gains electrons becomes reduced, going to a lower oxidation state [28]. Sodium borohydride (NaBH₄), hydrazine (N₂H₄), and sodium hypophosphite (NaPO₂H₂) are all common reducing agents. Figure 2.2 shows one possible reaction that results in the formation of iron nanoparticles from ferrous chloride and sodium borohydride in ethanol [29]. The reaction pictured is as follows;

\[
\text{FeCl}_2 + 2\text{NaBH}_4 + 6\text{C}_2\text{H}_6\text{O} \rightarrow \text{Fe} + 2\text{NaCl} + 2\text{B(OH)}_3 + 5\text{H}_2 + 12\text{CH}_4 + \text{Heat} \quad (2.8)
\]

There are many different byproducts in this reaction: boric acid, methane, sodium chloride, and hydrogen. There is the possibility that iron will switch between the Fe⁰ and Fe²⁺ state, as pictured by the double arrow, due to electron transfer between the iron atoms. As more iron is evolved, the iron will begin to cluster forming the nanoparticles. However, some boron will remain in the system and get absorbed into the nanoparticles. When a capping agent is applied, it
helps limit the growth of the nanoparticles. The capping agent is indicated by the serrated like boundaries.

The type of solvent in which the nanoparticles are suspended can influence the growth and properties of the nanoparticles. Water, while able to dissolve most metal salts that we would use in nanoparticle synthesis, has a propensity to carry dissolved oxygen, so particles suspended in water tend to instantly oxidize. This normally may be countered by adding extra reducing agent, and/or deoxygenating the water. However, water reacts with sodium borohydride in the following exothermic reaction [30]:

\[
\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2 + \text{Heat} \quad (2.9)
\]
This gradually reduces the concentration of reducing agent causing the particles to oxidize. Additionally, for nanotube manufacturing, water can inhibit growth of the nanotubes by evolving hydrogen and oxygen gases. The oxygen gas will oxidize the catalysts, eliminating all growth of nanotubes.

Ethanol is one of the more popular solvents for growing nanoparticles. Ethanol is able to dissolve many different kinds of metal salts. While ethanol reacts with sodium borohydride, it does so at a much slower rate than water. Because of this, the particles, if exposed to oxygen, can remain reduced for a longer period of time. Like water, ethanol reacts with sodium borohydride in the following reaction [31]:

$$\text{NaBH}_4 + 4\text{C}_2\text{H}_5\text{OH} \rightarrow \text{NaB(OC}_2\text{H}_5)_4 + 4\text{H}_2 + \text{Heat}$$  \hspace{1cm} (2.10)

However, because of the slower reaction rate, there can be a lot of boron contamination from sodium borohydride. Additionally, ethanol is a major fuel source for carbon nanotubes so it may be possible to add catalysts to the fuel prior to injecting it into the reactor.

Another possible solvent is butanol. Butanol is chemically similar to the other alcohols, but it does not react with sodium borohydride. However, the solubility of sodium borohydride is much lower than in ethanol or methanol. The tert-butanol isomer is able to dissolve 0.11 g of sodium borohydride per 100 g of solvent at room temperature, compared to ethanol and methanol being able to dissolve 4 g and 16.4 g respectively [32]. This causes it to have a very slow reaction speed in comparison to the other solvents. Since concentration of reactants is a contributing effect for nanoparticle growth, this can create a wider distribution of nanoparticle sizes. Additionally, butanol is a much more viscous solvent than ethanol or methanol. The higher the viscosity of the solvent, the longer it takes for the particles to coarsen, which can increase the size distribution [33]. One advantage of using butanol is that it is much less likely to evaporate when purging the system of
oxygen. This allows us to maintain the concentration of the iron salts in solution while reducing the amount of impurities that we would have to add to the system.

Methanol, while similar to ethanol in terms of physical properties, can make very different nanoparticles. Sodium borohydride reacts vigorously with methanol on contact by the following reaction:

\[ \text{NaBH}_4 + 4\text{CH}_3\text{OH} \rightarrow \text{NaB(OCH}_3)_4 + 4\text{H}_2 + \text{Heat} \]  \hspace{1cm} (2.11)

This reaction produces the salt sodium trimethoxyborohydride \[31\], which is insoluble in most solvents. Because of this reaction, experiments have a time constraint in order to create nanoparticles and the lifetime of the solutions are considerably shorter than their ethanol counterparts. However, because of the reaction rate, there is often much less boron contamination in the nanoparticles, making them better for producing carbon nanotubes than those produced in ethanol. With all other outside conditions being equal, methanol’s ability to dissolve sodium borohydride and its low viscosity causes it to have the fastest reaction rate with the smallest particle size distribution.

Boron contamination from sodium borohydride as a reducing agent has also been researched by Glavee et al \[34\]. By looking at the reduction of 10 mmol of ferric chloride in water with 6.0 mmol of sodium borohydride, an iron to boron ratio of 4.46:1 was observed. Similarly, with ferrous chloride the iron to boron ratio was 4.04:1. There is a distinct possibility that discrete amounts of iron boride form with this reaction. However, at around 400°C, the boron and iron starts to actively form the metalloid iron boride, which can drastically change the particles’ properties. This makes the nanoparticles less reactive for many industrial purposes, and creates a much harder substance than pure iron.
Another potential set of reducing agents are the polyphenols. Polyphenols are a category of chemicals that contain multiple carbon rings with hydroxide groups attached. An example of a polyphenol be seen in Figure 2.3, which is a chemical diagram for epigallcatechin gallate (EGCG). Most polyphenols are environmentally friendly, occurring naturally in many plants, such as tea. It is actually because of tea that we know that polyphenols can reduce iron [35]. When iron fortified sugar was first added to tea, the tea would change to a black color. This eventually started the research into this process. It is well known that polyphenols reduce a ferric ion to a ferrous ion, however, little is known about the reactions that could lead to zero valence iron. Several studies have looked at the use of green tea, and green tea extract, as reducing agents for iron [35,37]. However, because of the number of polyphenols, it is difficult to determine which play a role in which stage of the reduction process.

One particularly interesting category of polyphenols are the flavanols, such as epicatechin, and EGCG. They are some of the most abundant polyphenols, making up to 13% of the weight of green tea. They are also among the most reactive, as they have been shown to make the +3 to +2 reduction of iron [35]. Additionally, there may be many different reactions that lead to zero valence iron. Additionally, many reactions may not result in the production of iron nanoparticles. However, polyphenols seem to selectively reduce iron, while remaining a mostly inert chemical to other metals. This is most likely due to the energy levels inside the orbitals of the polyphenols matching the energy level needed to reduce the iron to its zero valance state [35,38]. As stated previously, polyphenols can also be used as a capping agent. Because of this, the use of polyphenols as a
reducing agent becomes very attractive for industrial purposes as it would reduce the number of toxic chemicals, and contaminants present inside the nanoparticles.

While each of the above solvents has different influences on nanoparticle synthesis, there is one major trend that reaches across all of the above solvents. The higher the temperature of the solvent, the faster the reaction rate. These reactions are likely to be first order and rates will follow a simple exponential temperature dependence. Depending on the surroundings of the nanoparticles, an increase in agglomeration size can occur as the nanoparticles will attract each other when they are in close proximity with each other.

2.4 pH Effects on Iron Nanoparticle Growth

Nanoparticle growth is heavily dependent on the pH of the solution. pH is defined as

\[-\log_{10}(a_{H})\] (2.12)

where \(a_{H}\) is the hydrogen activity inside the solution. For example, inside an acidic solution, hydrogen competes actively with other complexes or surfactants for sites on the iron nanoparticles. This allows for a large particle size distribution. Ostwald ripening can therefore occur at a greater speed, allowing for the nanoparticles to grow beyond their desired diameters. If the pH of the solution is extremely acidic, pH of 2.5 or below, the nanoparticles may not grow large enough for them to survive in solution. This is due to the competition for electrons with the excess protons that are present in an acidic solution [39]. Ultimately, this would cause them to dissolve back into the solution, rendering the solution ineffective.

An overly basic solution will also hinder the growth of iron nanoparticles. Over time, in a basic solution, the iron ions will undergo hydrolysis and become iron hydroxide. Iron hydroxide is unstable in solutions, especially at higher pHs. The hydroxides evolve hydrogen gas forming
iron oxides [40]. Any iron nanoparticles that do form, will be coated with an oxide shell, causing a larger size distribution of nanoparticles. This is enough to render the solution unsuitable, as it will hinder many of the aforementioned applications and will have vastly different properties than metallic iron nanoparticles.

Hydroxylation in water is much more likely to occur than with other solvents. For an Fe(III) ion, hydroxylation can begin at a pH as low as a pH of 1 and as high as 5, well within the range of an acid. Fe(II) is more resilient to hydrolysis and can survive in ion form up to pHs of 7 to 9 [22]. This would lead to iron oxide nanoparticle formation at pHs lower than otherwise would occur. Additionally, because of the loss in control in maintaining the iron ions, there would be a wider distribution of nanoparticle sizes due to oxide contamination occurring at different rates. In this case buffers have to be added. One example of such a buffer is citric acid which can buffer from a pH 3 to about pH 6 [41].

One way to help control the composition of a material in solution is to apply a voltage, $E_H$ to the system. The movement of the electrons due to the different applied voltages will make different materials the more energetically stable in solution. When $E_H$-$pH$ is plotted graphically, almost always at ambient temperature, it is known as a Pourbaix diagram. These diagrams usually assume a standard set of conditions: a water solution with a temperature of 25°C, at standard pressure, and a molar concentration of either 1 or $10^{-6}$ mols per liter of metal ions in solution [40]. The Pourbaix diagram of $10^{-6}$ iron can be seen in Figure 2.4. When a negative voltage is applied to the solution, electrons will leave the iron surface and discharge the ferrous ions, forming metallic iron (electroplating). This electron surplus also allows the iron to have an immunity to corrosion that normally occurs over time. Conversely, if a positive voltage is applied, the oxidation state of the iron increases. It is even possible to reach the iron (IV) state seen in FeO$_4^{2-}$ at the top of Figure
2.4. As the pH varies on the x-axis, a wide selection of states and compounds can be seen. Acidic solutions, where a surplus of hydrogen, or equivocal protons are present, will yield elemental iron or iron ions in solution. As the pH becomes more basic, or as OH\(^-\) ions or their equivalent become dominant in solution, hydroxides as well as negatively charged ions will be the most energetically stable in solution.

Iron reduction normally occurs at temperatures above 600°C in the presence of hydrogen. However, the temperature needed for the reduction of iron is suppressed to as low as 200°C with the addition of copper. Copper has much lower bond energy with another atom and therefore can be reduced at lower temperatures. For comparison, the bond energy of CuO and Cu\(_2\)O have enthalpies of formation of -155.2, and -166.7 kJ/mol respectively, while FeO, Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\) have values of -272, -822.2, and -1120.9 kJ/mol. Metallic copper can absorb hydrogen gas on its surface, where it will act as a hydrogen sink for iron alloyed with it. The close proximity of the hydrogen with the iron speeds up the reduction process that would normally occur at higher temperatures. This will help mitigate any problems associated with oxygen contamination [42].

![Pourbaix Diagram for 10^-6 Iron in water](image)

*Figure 2.4: Pourbaix Diagram for 10^-6 Iron in water [39]*
2.5 Parameters for Size Effects

Since concentration of the precursor salts is important to the size and growth of the nanoparticles, one needs to look at the forces acting on the solvent carrying the precursors and how these can change local concentrations. There are several different forces which affect the flow pattern of a droplet entering a large pool of liquid. The first force is referred to as the “stirring force” of the drop due to the momentum change from a free falling drop. This produces a downward motion. The curvature force occurs when the droplet is partially submerged, and is based off the internal pressures, or the curvature, of the droplet and pool. When the droplet enters the pool, a pressure gradient is formed as the droplet is assimilated into the pool. Since the curvature of the droplet almost always correlates to higher internal pressure in comparison to the bulk, the curvature force, which is created by the gradient, forces the droplet down into the bulk solution. The third is the buoyancy force. If the density of the droplet is greater than that of the pool, it will induce a net downward force. Similarly, if the density is smaller than that of the pool, it will induce an upward force [43].

The fourth force, known as the Marangoni force, occurs when the droplet is entering the pool. This force is completely dependent on the difference between the surface tension of the pool and the droplet. This leads to three scenarios: (1) when the surface tensions are equal, (2) when the droplet’s surface tension is greater, and (3) when the pool’s surface tension is greater. When the surface tensions are equal, there is no major contribution from this force. If the surface tension of the drop is greater than the droplet will pull the particles on the surface of the pool closer to it. This creates a chain reaction through the pool as a pressure is being equalized. The net force then provides a motion that essentially injects the droplet into the pool. The third case, when the surface tension is greater in the pool, the particles in the droplet are pulled away from the droplet and
towards the pool, creating an outward flow. This creates a distinctive swirling flow pattern along the edges of the container. These two cases can be seen in Figure 2.5. In Figure 2.5A, the surface tension of the droplet is higher than that of the pool around it. The downwards motion in A is caused by the Marangoni and stirring force. Upon impacting the wall at the bottom of the container, there is a swirling motion that occurs (E). C’ is the enclosing flow, where it fills the low pressure area, where the droplets fell. In Figure 2.5B, the downward motion is due only to the stirring force, while the rising motion (B) is due to the buoyancy and Marangoni forces. Eventually, the Maragoni forces move the droplets away from the center (C) until the flow impacts a wall forming a swirl (D). C’ is spreading flow, to account for the extra liquid that is added to the solution [43].

![Figure 2.5. Droplet motion when (A) the surface tension of the droplet is higher the solution and (B) the surface tension of the droplet is lower than the solution [43]](image)

The combination of these four forces can greatly affect the density of the precursor salt upon entering the solution. If the net force drag the droplets down into the solution, it is possible to have areas where very high concentrations of the salt fall straight through the media without diffusing very much. Conversely, if the net force is up, it will often make diffuse solutions under
the surface of the solvent that may not penetrate the full body of liquid during the nanoparticle synthesis process. In both cases, this results in non-uniform growth of the nanoparticles, and local exhaustion of the reducing agent. One way of ensuring that there is more uniformly mixing in both cases is to constantly keep solution mixing with an electronic stirrer or with a gas to minimize these effects.

Many of the variables that go into the synthesis of zero valence iron have been studied. Hwang et al. [44] has examined three different parameters in the reduction of ferric chloride by sodium borohydride: (1) reducing agent delivery speed, (2) reducing agent concentration, and (3) precursor concentration. It is important to note that each one of these parameters is measured independently. For the sodium borohydride delivery rate, they looked at speeds of 2, 5, 10, and 20 ml/min. There is very little difference in the size of the nanoparticles at the lower delivery rates, but there is a rapid decrease in size as the reducing agent is delivered faster, from 87.4 to 9.5nm. However, the size of the aggregate of the nanoparticles increased at the faster rates from 1,376 to 55,787 nm. This is because of an increase in magnetic force between the nanoparticles as the particles are formed in close proximity to each other. Hwang et al. also report that at lower reducing agent flows more spherical particles formed. At faster flows, the nanoparticle whiskering, where thin strands of metal form instead of spherical nanoparticles, can be observed. The nanoparticles became smaller as the concentration of sodium borohydride increased. The same occurs with higher concentrations of the precursor, ferric chloride. One other consequence of higher concentrations of iron precursor is that with more iron salt, there is more of a chance that iron whiskers will form. All of these results assume that the particles were aged in the solution for 20 minutes, which could allow for different nanoparticle ripening processes to occur.
Zin et al. [20] studied the particle size for zero valence iron-copper nanoparticles by varying the concentration of copper chloride added to the solution. They looked at copper to iron weight ratios from 1:5 to 1:20. They found that the particle size decreased from 85.15 nm from the highest copper concentration to 44.58 nm at the lowest concentration. They noticed the same aggregation of nanoparticles as Hwang et al., however, they reported that the average aggregate size increased with lower copper contents, which suggests that a copper coating helps keep the particles separated from each other. This study also shows that sodium borohydride produces smaller nanoparticles than potassium borohydride, at 60 and 80 nm respectively. In this study all particles were aged for an extra ten minutes.
Chapter 3: Experimental Procedures

3.1: The Iron Compounds

Throughout this work two different salts are used to produce iron nanoparticles: ferrous chloride, and ferric nitrate. These salts were selected for their solubility in alcohols. Upon reaction, the chlorine typically forms either another salt, or small amount of hydrochloric acid as an intermediate to forming another salt. In either case, it is fairly innocuous for industrial applications and can be removed by decantation, or allowed to remain inside of the system. Ferric chloride is an air stable compound which upon being dissolved into an alcohol retains its +3 valance state. However, it requires more reducing agent to reduce to the zero valence state. The reducing agent required would create more impurities than when used with the lower oxidation state salt, ferrous chloride. A disadvantage to ferrous chloride is that it cannot be exposed to oxygen or water vapor for an extended period of time as it will tend to form ferric chloride. This occurs by the following reactions.

\[
2\text{FeCl}_2 + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 4\text{HCl} + \text{H}_2 \quad (3.1)
\]

\[
2\text{FeCl}_2 + 2\text{HCl} \rightarrow 2\text{FeCl}_3 + \text{H}_2 \quad (3.2)
\]

Therefore, ferrous chloride if not used immediately in solution, can result in a lower, less uniform yield of nanoparticles. The ferrous chloride tetrahydrate came from Acros organics.

Ferric nitrate is more soluble in most solutions than both chloride salts. However, ferric nitrate decomposes below 400°C into iron oxides and nitrogen oxides. The iron ion can be captured by a capping agent, which will isolate the iron from the oxygen and may reduce it further. This allows coated uniform iron particles to be produced at lower temperatures than would be required.
for other salts. The ferric nitrate salt that we use is obtained in nonahydrate form from Acros organics.

The reducing agents used were Chinese Green Tea (CGT), Bigalow Green Tea, Polyphenon-60 and sodium borohydride. The Polyphenon-60 was obtained from Sigma-Aldrich. The sodium borohydride came from Acros Organics.

3.2 Reflux Preparation

A single neck flask, pictured in Figure 3.1 is filled with the appropriate amounts of ferric nitrate nonahydrate and hexadecylamine in a 1:5 molar ratio. A water cooled condenser is placed in the neck of the flask. The inlet and outlet of the condenser are connected to a water chiller that is set to be just above the freezing point. The apparatus is placed inside a half spherical mantel with a thermocouple underneath the three neck flask. The flask’s base is wrapped in fiberglass insulation. The top of the condenser, and the remaining necks of the flask are capped with a septum. The entire apparatus is then purged with an inert gas, which is typically nitrogen. The heating mantel is turned on and heated to 340-360 °C. After 30 to 60 minutes, the hotplate is turned off and cooled to room temperature. By this point, a black, waxy substance has conglomerated at the bottom of the flask. By adding a solvent, such as methanol, ethanol or hexane, this wax goes into suspension and can potentially be used for nanotube forest growth, where the hexadecylamine can be removed.
Figure 3.1: Reflux Experimental Apparatus
3.3 Polyphenol Preparation

A polyphenol source, such as green tea or green tea extract, or polyphenon-60 is added to a solvent, and stirred. It is then heated or cooled to the desired temperature. The resulting mixture is then filtered several times to remove any large solid contaminants. To increase the concentration of the polyphenols, some of the solvent can be boiled off. The iron salt, either ferric or ferrous chloride, is then added to this solution. The solution turns black with a green tint. Once again, it is filtered and is ready for characterization and application. The mass of the dried polyphenol solution is measured to determine the approximate amount of the chemicals in solution.

3.4 Sodium Borohydride Sealed Flask Preparation

A three or four neck flask is filled with a solvent with either dissolved sodium borohydride or an iron salt. It is then sealed with septa that are fastened to the flask itself. On one neck of the flask, a gas line is inserted using a needle which penetrates over a centimeter into the solution below. This needle allows the flask to be purged, and agitates the solution. On the opposite side, a smaller needle is inserted that stays above the liquid. It is connected to a line that runs into a flask of water, which allows gas to flow out, and keeps outside gases from diffusing into the system. Additionally, a pump line can be run through the center which would allow for the solution to be pumped out. All chemicals are added to the system via syringe so that the oxygen content can be kept to a minimum inside the apparatus.
3.5 Particle Characterization

Once synthesis is complete, the nanoparticles can be mounted for use in a transmission electron microscope (TEM). The TEM for this experiment was a Zeiss/LEO 922 Omega TEM used at an accelerating voltage of 120kV with a resolution line of 0.12nm. When nanoparticle formation is confirmed, the images are processed using ImageJ to find average particle size and to create a histogram of particle diameters. Electron diffraction from the TEM can be used to see the orientations of the nanoparticles as well as help identify the elements present.

That the nanoparticles are iron was confirmed by X-ray diffraction also used to measure other impurities that might be present. Additionally, x-ray diffraction will allow us to determine the allotrope of the iron present in the nanoparticles.

A scanning electron microscope (SEM) can also be used to obtain a more detailed image of the nanoparticles and nanotubes. Additionally, energy dispersive spectroscopy (EDS) can be used to identify any elements that are present in the nanoparticles. We use a Tescan SEM.

3.6 Nanotube Production

In floating catalyst chemical vapor deposition (CVD), a nanoparticle solution is pumped into a vented tube furnace. The solution typically contains a sulfur source, such as thiophene or carbon disulfide. This solution is nebulized to form a spray of droplets with a combination of hydrogen, nitrogen, ammonia, helium and/or argon. With a temperature between 1200 °C and 1500 °C, the hydrogen and ammonia are able to reduce any oxygen or organic compounds on the surface of the nanoparticles. As the carrier liquid evaporates and decomposes, the following occurs according to temperature: (1) ethanol or another carbon source (methanol, butanol, benzene, etc) break down thermally into many carbon subspecies (CH₃, C₂H₃, etc), (2) these subspecies absorb
onto the surface of the nanoparticles, (3) hydrogen is then released, (4) the catalysts gradually become saturated with carbon, until the growth of the carbon nanotube commences.

Forest growth of nanotubes is similar to CVD growth. The catalysts are deposited onto a substrate prior to entering a reaction chamber. A hydrogen gas, mixed with argon, is used to reduce the catalysts on the substrate and purge the chamber of oxygen. It is then heated to 750 °C to 1000 °C. A fuel source, such as ethanol, is added in gaseous form. As the fuel is broken down, it is deposited onto the surface of the catalysts and the nanotubes grow attached to the substrate. In many cases, the nanotubes grow in the same direction, making it look like a forest.
Chapter 4: Experimental Results

In this chapter we present the experimental results from our trials. We will discuss the meaning of our findings in the following chapter.

4.1: Hexadecylamine Reflux Synthesis

Nanoparticles were successfully formed using an iron nitrate reflux reaction with hexadecylamine. Figure 4.1 is a TEM image of the particles. The image has many splotches that can be attributed to the hexadecylamine contamination of the grids. The nanoparticles seem to cluster together in some regions, however, they tend to remain as independent structures rather than as single agglomerations. A selection of 50 nanoparticles has yielded an average particle size of 6.5 nm with a standard deviation of 1.3 nm. A histogram of these sizes can be seen in Figure 4.2. In this figure, all sizes were rounded to the nearest integer. At the same time that Figure 4.1 was taken, an electron diffraction pattern was obtained. The electron diffraction pattern can be seen in Figure 4.3. In this figure, one can see two electron diffraction lines close together followed by one that is alone. This is an electron diffraction pattern that is reminiscent of an FCC crystal structure, which is atypical for iron at standard temperature and pressure.
Figure 4.1: TEM image of Hexadecylamine Coated Iron Nanoparticles
Figure 4.2: Histogram of 50 Hexadecylamine Coated Iron Nanoparticles

![Histogram of Hexadecylamine Coated Iron Nanoparticles](image)

Figure 4.3: Electron Diffraction Pattern of Hexadecylamine coated Iron Nanoparticles

![Electron Diffraction Pattern](image)
4.2: Ferrous Chloride-Polyphenol Synthesis

Nanoparticles were formed using ferrous chloride inside a polyphenol reducing agent mixture. The solution was made so that there would be 0.5 g/L iron in this sample. Figure 4.4 is a TEM picture of these nanoparticles. Unlike the particles produced in hexadecylamine, these nanoparticles seem to avoid agglomeration. However, some of these nanoparticles seem to have a darker core, followed by a lighter band along the outside. This may indicate the presence of a coating on the nanoparticles, or more concentrated iron in a subsection of the particle. A dark field image can be seen in Figure 4.5. The bright spots correspond to an electron diffraction ring inside Figure 4.7. This indicates that these nanoparticles have a crystalline nature. Figures 4.4 and 4.5 combined, suggest that some of the larger nanoparticles are actually groupings of grains in different orientations, as only sections of these particles are illuminated. The average size of the nanoparticles produced in this method is 6.1 nm in diameter with a standard deviation of 1.6 nm, as shown in Figure 4.6.

A temperature comparison trial was run using Bigalow Green tea. Three samples were prepared at 0 °C, 25 °C and 75 °C at a concentration of 0.5 g/L. Figure 4.8 is an image of the particles obtained at 0 °C. The shape of some of the nanoparticles is different from both of the aforementioned processes, where some of the nanoparticles appear to be more rod-like. Figure 4.9 is a histogram of 50 spherical nanoparticles. The particles are much larger than in the previous trial, with an average diameter of 15.78 nm. Similarly, the distribution is larger with a standard deviation of 3.60 nm.
Figure 4.4: TEM image of Polyphenol Coated Iron Nanoparticles
Figure 4.5: Dark Field Image of CGT Polyphenol Coated Iron Nanoparticles
0.94 g/L Polyphenol - 0.5 g/L Iron Nanoparticles (I)

Avg: 6.1 nm  Std Dev: 1.6 nm

Figure 4.6: Histogram of 50 CGT polyphenol coated iron nanoparticles from 0.5 g/L iron solution

Figure 4.7: Electron Diffraction Pattern from CGT Polyphenol Coated Iron Nanoparticles
Synthesis and Characterization of Iron Nanoparticles

Figure 4.8: 0.5g/l Iron Nanoparticles Created at 0°C in Bigalow-Ethanol Tea

Figure 4.9: Histogram for 0.5g/l iron nanoparticles at 0°C in Bigalow-ethanol tea
An image of the 25 °C run can be seen in Figure 4.10. In comparison to the 0 °C nanoparticles, there are far less rod like nanoparticles. However, there are minor aggregations of nanoparticles that appear. The related histograms for this image is shown in Figure 4.11 where the average diameter of the nanoparticle is 15.2 nm with a standard deviation of 3.6 nm. This is comparable to the previous sample.

An image of the 70 °C nanoparticles can be seen in Figure 4.12. The particles are smaller than either of the two previous trials, with an average of 13.1 nm in diameter, seen in Figure 4.13. However, the standard deviation of the nanoparticles is slightly higher at 3.7 nm, which is comparable to the two previous trials. There appears to be some minor agglomerations of nanoparticles.

The effect of concentrations of iron and polyphenols on the size of nanoparticles is next studied. Three different solutions with, 0.1 g/L, 0.5 g/L, and 2.5 g/L of iron were produced from ferrous chloride with the same solution 0.94 grams of polyphenols. The 0.5 g/L and 2.5g/L were then compared to the same concentrations made in a solution of 1.5 g/L polyphenols. The 0.1g/L solution can be seen in Figure 4.14. Inside the image, there are several large nanoparticles, above 20 nm in diameter, that are surrounded by smaller nanoparticles. The smaller nanoparticles have nearly identical appearance. There are no internal patterns, or grain boundaries, indicating that these are most likely single domain nanoparticles. A histogram of nanoparticles can be seen in Figure 4.15. They have an average size of 6.0 nm and a standard deviation of 1.8 nm. Nanoparticles larger than 12 nm were discounted in this histogram due to them most likely being due to ripening processes, or closely packed agglomeration of nanoparticles.
Figure 4.10: 0.5g/l Iron Nanoparticles at 25°C in Bigalow-Ethanol Tea

Figure 4.11: Histogram for 0.5g/l Iron Nanoparticles at 25°C in Bigalow-Ethanol Tea
Synthesis and Characterization of Iron Nanoparticles

Figure 4.12: 0.5g/l Iron Nanoparticles at 70°C in Bigalow-Ethanol Tea

Figure 4.13: Histogram for 0.5g/l Iron Nanoparticles at 70°C in Bigalow-Ethanol Tea
Synthesis and Characterization of Iron Nanoparticles

Figure 4.14: Nanoparticles made from 0.1g/L iron with 0.94 g/L CGT polyphenols

Figure 4.15: Histogram of nanoparticles made from 0.1g/L iron with 0.94 g/L CGT polyphenols

Polyphenol - 0.1g/L Iron Nanoparticles

Avg: 6.0 nm  Std Dev: 1.8 nm
The nanoparticles produced with 0.5 g/L iron and 0.94 g/L polyphenol can be seen in Figure 4.16. We see a central location of larger nanoparticles, surrounded by much smaller nanoparticles. Similarly, the smaller nanoparticles are mostly uniform in appearance, with very few being much darker than the others. However, the larger nanoparticles that are present have begun to show some interesting patterns, including dark lines running down the center, and double triangles. This indicates that they are multi-domain nanoparticles and are in different crystal orientations. A histogram of the smaller nanoparticles can be seen in Figure 4.17. The particles have an average diameter of 5.8 nm with a standard deviation of 1.2 nm. This makes the nanoparticles slightly smaller more monomodal than the similar run seen in Figure 4.4.

The 2.5 g/L iron nanoparticles produced in 0.94 g/L polyphenols can be seen in Figure 4.18. The larger nanoparticles that are seen in this image have several dark areas inside the image. There are several nanoparticles that have one or more dark lines that run through them. These nanoparticles are also multi-domain and represent cryptographic twinning. Another image of these nanoparticles can be seen in Figure 4.19. Some of these nanoparticles clearly have three fold symmetry, as they appear to be more triangular than the nanoparticles seen in the previous images. Both of these images have a lot of background features that are not nanoparticles. This is most likely due to unreacted ferrous chloride that is present in the sample. Because of this, most of the smaller nanoparticles, cannot be discerned from background features. A histogram of 50 of the nanoparticles can be seen in Figure 4.20. The nanoparticles have an average diameter of 16.3 nm with a standard deviation of 2.8 nm, making them much larger in size and distribution than the other two trials made with the same solution of polyphenols.
Figure 4.16: Nanoparticles made from 0.5g/L iron with 0.94 g/L CGT polyphenols

Figure 4.17: Histogram of nanoparticles made from 0.5g/L iron with CGT 0.94 g/L polyphenols

Polyphenol 0.5 g/L Iron Nanoparticles

Avg: 5.8 nm Std. Dev: 1.2 nm
Figure 4.18: Nanoparticles made from 2.5 g/L iron with 0.94 g/L CGT polyphenols
**Figure 4.19:** More nanoparticles made from 2.5g/L iron with CGT 0.94 g/L polyphenols

**Figure 4.20:** Histogram of nanoparticles made from 2.5g/L iron with 0.94 g/L CGT polyphenols

Average: 16.3 nm  
Standard Deviation: 2.8 nm
The 0.5 g/L nanoparticles made with 1.5 g/L of polyphenols can be seen in Figure 4.21. The nanoparticles are grouped by size as those in Figure 4.16. Instead, the medium sized (~10 nm) nanoparticles are more evenly spread out with the smaller nanoparticles, while the larger, 20 nm particles have disappeared. Like the previous images, the larger sized nanoparticles have dark lines, and spots inside of them, while the smaller nanoparticles are mostly uniform. Figure 4.22 is a histogram of the nanoparticles seen in Figure 4.21. The average particle size and broader distribution than those in Figure 4.16, at an average of 8.5 nm with a standard deviation of 2.9 nm. However, the plurality of the nanoparticles seem to be around 6 nm in diameter. The histogram also seems to be split into two regions: one focused around 6 nm and another around 11 nm in diameter.

The nanoparticles produced with 2.5 g/L iron and 1.5 g/L polyphenols can be seen in Figure 4.23. Like Figure 4.18, there are background features that are not nanoparticles, keeping the smaller nanoparticles obscured. The larger nanoparticles can still be seen with the same features that are present in the other images. The histogram for the nanoparticles in Figure 4.23 can be seen Figure 4.24. The average diameter for these nanoparticles is 7.4 nm with a standard deviation of 1.4 nm. These nanoparticles are considerably smaller than the ones from Figure 4.18, where the average was 16.3 with a standard deviation of 2.8 nm.
Figure 4.21: Nanoparticles made from 0.5g/L iron with 1.5 g/L CGT polyphenols

Figure 4.22: Histogram of nanoparticles made from 0.5g/L with 1.5 g/L CGT polyphenols

Increased Polyphenol - 0.5 g/L Iron Nanoparticles

Avg: 8.5 nm  Std. Dev: 2.9 nm
Figure 4.23: Nanoparticles from 2.5 g/L Iron with 1.5 g/L CGT polyphenols

Increased Polyphenol - 2.5 g/L Iron Nanoparticles

Avg: 7.4 nm  Std Dev: 1.4 nm

Figure 4.24: Histogram of nanoparticles from 2.5 g/L Iron with 1.5 g/L CGT polyphenols
The results of an infrared absorptometer measurement to better understand the chemistry behind the formation of the nanoparticles can be seen in Figure 4.25. This spectrum suggests that there is a lack of C=O. This bond which is present in ECGC and many other polyphenols, would normally appear at around 1750 cm\(^{-1}\). The four bonds that are most present are the O-H bond at 3300 cm\(^{-1}\), the C-H bond at 3000 cm\(^{-1}\), the aromatic C=C bonds between 1500 and 1250 cm\(^{-1}\), and the very strong C-O bond peak at 1000 cm\(^{-1}\).

An x-ray spectrum of these nanoparticles can be seen in Figure 4.26. This experiment was run at a 10 g/L iron concentration and 3.3 g/L of Polyphenon-60 as a reducing agent at room temperature. A run was done with 0.5 g/L iron with 1.5 g/L polyphenols, however, the polyphenols obscure the iron in the sample due to the difference in abundance. The nanoparticles in this experiment were centrifuged from solution, and washed with ethanol to remove excess ferrous chloride. The x-ray diffraction spectrum does not show any peaks for BCC iron. Instead, we see three peaks for FCC iron. These peaks can be seen at the 2\(\theta\) values of 43.54, 49.80, and 74.26. Aluminum oxide makes up the remaining peaks in the spectrum, including having a slight overlap on the 43.38 and the shoulder on the 74.25 2\(\theta\) peaks. The only peaks that are unidentified are at the 42.97 and 66.09 2\(\theta\) values. These are most likely peaks from the polyphenol-iron complex that competes with nanoparticle formation.

A second x-ray diffraction pattern of polyphenol reduced nanoparticles can be seen in Figure 4.27. This sample was prepared from the same batch as those in Figure 4.26 only the spectrum was recorded after baking at 250 °C for fifteen minutes. Unfortunately, the polyphenol oxidized and in the process removed some of the nanoparticles. However, some of the BCC peaks can be seen at 44.70 and 65.19 2\(\theta\). The FCC peaks are still present though at a diminished intensity. Several other new peaks can be seen in comparison to the room temperature produced x-ray
spectra. These peaks are all due to iron oxide which has formed since the polyphenols that were keeping the iron form oxidizing have been removed.
Figure 4.25: Infrared transmittance spectra of polyphenol coated nanoparticles
Figure 4.26: X-ray diffraction pattern of 10 g/L iron nanoparticles at 25 °C in standard and log scales
Figure 4.27: X-ray diffraction pattern of 10 g/L iron nanoparticles at 250 °C in standard and log scales
4.3: Sodium Borohydride Reduced Synthesis

The sodium borohydride synthesized iron nanoparticles can be seen in Figure 4.28. The nanoparticles are very small, but they tend to form very large, nonsymmetrical agglomerations. A histogram of 50 nanoparticles can be seen in Figure 4.29. The average size of the nanoparticles is 4.8 nm, with a standard deviation of 0.6 nm.

Another batch of sodium borohydride reduced iron nanoparticles can be seen in Figure 4.30. These particles have three iron weight percent copper added to them. These nanoparticles are much more uniformly distributed throughout the image, and do not seem to be agglomerating as much as the nanoparticles without iron. A histogram of 50 of these nanoparticles can be seen in Figure 4.31. These are the smallest nanoparticles in this work at 3.9 nm average diameter with a standard deviation of 0.7 nm.
Figure 4.28: Nanoparticles made with 0.5 g/L concentration iron with sodium borohydride from ferrous chloride

Figure 4.29: Histogram of Sodium Borohydride Produced, 0.5g/L Iron Nanoparticles
Synthesis and Characterization of Iron Nanoparticles

Figure 4.30: Nanoparticles made with 0.5 g/L concentration iron with sodium borohydride from ferrous chloride with 3 iron wt% copper.

Figure 4.31: Histogram of sodium borohydride reduced, 0.5g/L iron nanoparticles with 3wt% Cu
4.4: Nanotube Production

Using nanoparticles produced with sodium borohydride and 0.5g/L iron, we conducted carbon nanotube/nanofiber forest growth experiments. The first set of nanoparticles was produced in ethanol with a 0.5 g/L concentration of iron, from ferrous chloride, on an alumina substrate. A SEM image of this sample can be seen in Figure 4.32. There is minimal fiber growth with this sample, and it appears the larger particles have formed. In comparison, a batch of similar nanoparticles were produced in methanol, which produced the image seen in Figure 4.33. This substrate has had significant fiber growth. The fibers are about 200 nm in diameter, and are several micrometers long. They are mostly straight fibers, with an occasional rounded section towards the end, which could be a collection of catalyst particles.

Figure 4.32: Carbon Nanotubes grown with NaBH4 reduced iron nanoparticles in ethanol
Figure 4.33: Carbon nanotube forest grown with NaBH4 reduced iron nanoparticles in methanol
Chapter 5: Discussion

For convenience, the average diameter, standard deviation, and error, which is to be discussed in this chapter, of the nanoparticles are presented in Table 5.1 below.

Table 5.1: Average diameters, standard deviation and size error of nanoparticle samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Diameter (nm)</th>
<th>Standard Deviation (nm)</th>
<th>Error in Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexadecylamine</td>
<td>6.45</td>
<td>1.29</td>
<td>0.18</td>
</tr>
<tr>
<td>0.5g/L Fe - Polyphenol 0.94 g/L (1)</td>
<td>6.07</td>
<td>1.59</td>
<td>0.22</td>
</tr>
<tr>
<td>Bigalow 0°C</td>
<td>15.78</td>
<td>3.60</td>
<td>0.51</td>
</tr>
<tr>
<td>Bigalow 25°C</td>
<td>15.20</td>
<td>3.64</td>
<td>0.51</td>
</tr>
<tr>
<td>Bigalow 70°C</td>
<td>13.20</td>
<td>3.72</td>
<td>0.53</td>
</tr>
<tr>
<td>0.1 g/L Fe - 0.94 g/L Polyphenol</td>
<td>5.95</td>
<td>1.83</td>
<td>0.26</td>
</tr>
<tr>
<td>0.5 g/L Fe – 0.94 g/L Polyphenol (2)</td>
<td>5.76</td>
<td>1.23</td>
<td>0.17</td>
</tr>
<tr>
<td>2.5 g/L Fe – 0.94 g/L Polyphenol</td>
<td>16.27</td>
<td>2.83</td>
<td>0.40</td>
</tr>
<tr>
<td>0.5 g/L Fe – 1.5 g/L Polyphenol</td>
<td>8.46</td>
<td>2.90</td>
<td>0.41</td>
</tr>
<tr>
<td>2.5 g/L Fe - 1.5 g/L Polyphenol</td>
<td>7.37</td>
<td>1.44</td>
<td>0.20</td>
</tr>
<tr>
<td>0.5 g/L Fe - Sodium Borohydride</td>
<td>4.81</td>
<td>0.64</td>
<td>0.09</td>
</tr>
<tr>
<td>0.5 g/L Fe 3wt% Cu - Sodium Borohydride</td>
<td>3.86</td>
<td>0.66</td>
<td>0.09</td>
</tr>
</tbody>
</table>

5.1 Hexadecylamine Reflux Synthesis

At the time of their measurement, these nanoparticles were over seven months old, making them the oldest nanoparticles measured. Their long shelf life is most likely due to the size of the hexadecylamine and ability to separate the nanoparticles from each other. The electron diffraction in Figure 4.3 pattern does have the characteristic look of an FCC pattern, where there are two close electron diffraction lines followed by one farther away. There is a slight chance that this may be
the result of ferrous oxide (FeO), which has a FCC rocksalt pattern. However, FeO is not stable below 575 °C, and will slowly decompose to magnetitite (Fe₃O₄) and ferric oxide (Fe₂O₃) [45]. Because of the clarity diffraction pattern lines, it is most likely FCC iron. However, as the multihued Figure 4.1 suggests, the hexadecylamine has a very waxy texture to it making it very difficult to characterize and use in applications. Additionally, hexadecylamine is toxic, making it less appealing for applications. For these reasons, the composition of these nanoparticles was not fully determined.

5.2 Ferrous Chloride-Polyphenol Synthesis

The nanoparticles that are produced by the chemical reduction of ferrous chloride and polyphenols have produced a wide range of characteristics. The nanoparticles for the 0.5 g/L iron 0.94 g/L polyphenol sample were 6.07 nm average in diameter with a standard deviation of 1.59 nm. When comparing the light field and dark field images in Figures 4.4 and 4.5, we see that several different nanoparticles are illuminated in Figure 4.5. Of particular interest is the two neighboring nanoparticles that are illuminated on the top right. One has a much darker core than the other. This indicates that there are several different morphologies that are being yielded during this process. When examining the large center nanoparticle, only a portion of it is illuminated under the electron beam. These nanoparticles are aggregates of smaller nanoparticles that have merged together due to ripening processes.

The electron diffraction pattern for the 0.5 g/L iron 0.94 g/L polyphenol sample in Figure 4.7 for this sample has an FCC nature to it. However, unlike the hexadecylamine nanoparticles, the diffraction rings are far less crisp. The rings are dull with bright spots that occasionally appear inside of them. Looking at the light and dark field images again, there are nanoparticles that are
speckled under the electron beam. These smaller nanoparticles are also aggregates of even smaller nanoparticles that are separated by some other media. It is possible that these small grains in the nanoparticles are being separated by polyphenols or other smaller grains of iron.

The Bigalow Tea experiments serve two purposes, the first is to look at the dependence on different polyphenol sources as well as the temperature dependence for nanoparticle growth. Comparing Figures 4.4 to any of the Bigalow tea experiments, one sees a dramatic increase in diameter of the nanoparticles. There are two possibilities for this change in diameter, the first is that there is less of the polyphenols to coat the nanoparticles. The nanoparticles increase in size, decreasing the surface area that the polyphenols have to coat. The second possibility, is that there are more of different polyphenols that would direct the reduction to elemental iron through a different chemical path.

The trend seen as the nanoparticles were formed from 0°C to 70°C is that the nanoparticles became smaller, with a slight increase in the standard deviation. Similarly, the reaction that forms the nanoparticles happens at a faster rate at a higher temperature. The size difference between these three sets of nanoparticles is at least partly due to ripening processes. Since the 0°C sample takes longer for the reaction to go to completion, some nanoparticles are formed earlier than others. As new nanoparticles are formed, they are absorbed into the older, larger nanoparticles due to Ostwald ripening. The reaction occurs faster in the higher temperature trials due to the iron ions and particles having increased movement due to the thermal energy. This leads to more competition for the nanoparticles during the Ostwald ripening phase, as the nanoparticles will encounter a more uniform amount of iron to absorb. This results in smaller nanoparticles being formed.

Concentration of both the polyphenols and the iron present in the system has had a major effect on the size of the nanoparticles. Looking at the average diameter of the nanoparticles from
the 0.1g/L Fe to the 0.5 g/L Fe, we see a statistically insignificant decrease in the diameter of the nanoparticles, and a 33% reduction of the standard deviation. Like the temperature trial, this may be partially due to Ostwald ripening. In the lower concentration sample, the nanoparticles will not encounter each other at the same rate as the nanoparticles in one with a higher concentration. Some of the nanoparticles will encounter more iron than others, leading to a larger distribution of nanoparticle sizes. As more iron is added to the solution in these low concentrations, the nanoparticles become increasingly likely to encounter the same amount of iron, narrowing the size distribution of the particles.

The average diameter and standard deviation of the nanoparticles increases from the 0.5g/L to 2.5g/L iron nanoparticles. The increase in diameter is in part due to the relative abundance of iron that can be absorbed into the nanoparticles. The excess iron would allow Ostwald ripening to occur for a longer period of time, creating larger nanoparticles. However, the crystallographic background of Figure 4.19 suggests that the increase in diameter and standard deviation are also in part due the complete utilization of the reduction potential of the polyphenols. If the polyphenols are being used to completion, they would not be able to act as efficiently as a capping agent for the iron producing a larger size nanoparticle.

There is a slight size difference between the first and second 0.5 g/L iron 0.94 g/L polyphenol samples, where one has an average of 6.07 ± 0.22 nm in diameter while the other has a 5.76 ± 0.17 nm diameter. The sample with 6.07 nm average was about three weeks old when it was prepared for the TEM, while the second one was prepared 10 minutes in advance to being put onto the TEM grid. This allowed for more time for Ostwald ripening to occur.

The 0.5 and 2.5 g/L were then produced in a 1.5g/L polyphenol concentration. The increase in average size of the nanoparticle for the 0.5 g/L in Figure 4.21 could indicate a difference in
reduction method of the polyphenols for iron. With the increase in polyphenols, it is possible that an alternative chemistry for reduction and capping of nanoparticles becomes prevalent. In comparison, the particles seen in the 2.5 g/L concentration have undergone a 55% reduction in average size. This suggests that the larger nanoparticles in Figures 4.18 and 4.19 are caused by a lack of polyphenols rather than by a higher concentration of polyphenols.

The infrared absorption spectrum of 0.5 g/L iron with 1.5 g/L suggests a lack of carbon double bonded to oxygen. This is a very prominent bond in many of the polyphenols such as EGCG. The lack of a strong absorption peak suggests the polyphenols with this kind of bond are playing an active role in the reduction of iron.

5.3 Morphology of Polyphenol Coated Nanoparticles

Many of the nanoparticles seen in chapter 4 have very unique patterns that are present inside the particles themselves. One of the best examples is the bowtie shape that is seen in the 0.5g/L concentration of nanoparticles of Figure 4.16 is presented here as Figure 5.1. This bowtie shape is known to be caused by icosahedral twinning in FCC crystals [46]. A crystal twin occurs when two different oriented crystals meet and match orientations at a single plane. For FCC crystals, the work of formation is lowest for tetrahedral crystal formation. As these tetrahedrons form, they assemble together to form an icosahedron structure, especially at sizes of 10’s of nanometers or smaller. These icosahedral nanoparticles are the most stable form of iron at sizes below 11 nm, but can still exist at larger diameters [47]. Another possible pattern that can be seen with icosahedron
nanoparticles can be seen in Figure 5.2 from the 2.5g/L iron concentration in Figure 4.19. This is a threefold symmetrical pattern indicated by three dark spots on the nanoparticles.

Decahedral FCC nanoparticles can also be seen in several of the nanoparticles. Decahedral particles become the most energetically stable at diameters of between 16 and 50nm. A characteristic, star pattern, with fivefold symmetry is the most common indication of these nanoparticles. An example can be seen in Figure 4.19 with the 2.5 g/L iron of nanoparticles. One example from this image can be seen in Figure 5.3. The nanoparticle is slightly tilted obscuring one of the arms from the star shape. Like the icosahedral crystals of smaller diameters, these are also made up of twins from tetrahedral FCC crystals [47].

Another pattern that appears in the nanoparticles can be seen in Figure 5.4A. This nanoparticle taken from Figure 4.15 has a single twinned line that is visible down the center of it, giving it twofold symmetry. The particle will typically appear to be two different shades on either side of the boundary. The particle is 15.9 nm in diameter, making it most likely a decahedral particle. If the particle has enough defects, there
can be more than one boundary that forms such as the one seen in Figure 5.4B from Figure 4.19.

While the x-ray spectrum does show that the nanoparticles are FCC, the accepted value for the diffraction peaks differs from what was seen in the samples. For FCC, the peaks would normally appear at the 2\(\theta\) values of 43.38, 50.52 and 74.26. These peaks would correspond to the (111), (200), and (220) crystal planes respectively. We see the peaks at 43.54, 49.80, and 74.25 2\(\theta\). This difference in the x-ray spectra peaks suggests that the FCC lattice of the iron is being deformed, most likely by carbon or some other product from the reaction that formed these nanoparticles. Using Bragg’s law:

\[ n\lambda = 2d\sin(\theta) \]  

(5.1)

Where “\(\lambda\)” is the wavelength, “d” is the interplanar spacing, “\(\theta\)” is the angle of incidence and “n” is a positive integer related to the order of diffraction. If we rearrange and assume there are no interplanar diffractions, “n” is equal to one, we get the equation:

\[ d = \frac{\lambda}{2\sin(\theta)} \]  

(5.2)

When we set the wavelength to the wavelength for Cu-K\(\alpha\) x-rays, 1.5418 Å, we get the value of the interplanar spacing for the (111), (200), and (220) are a 2.08, 1.83, and 1.28 Å respectively. In comparison, the accepted values for (111), (200), and (220) peaks are 2.09, 1.81, and 1.28 Å.

We are able to convert the interplanar spacing to the lattice parameter with the relation:

\[ d = \frac{a}{\sqrt{h^2+k^2+l^2}} \]  

(5.3)

In equation 5.3, “a” is the lattice parameter, and “h”, “k”, and “l” are the Miller indices. Using the three peaks that have been observed, we find that the lattice parameters given by the (111) is 3.60 Å, 3.66 Å for the (200) and 3.62 Å for the (220) planes. Using the accepted value for FCC iron, we find the lattice parameter to be 3.62 Å. Only two of the three sides of the crystal are
distorted. This means that the impurities are resting inside some of the octahedral sites on the crystal lattice, which for the FCC structure, are in the center of the crystal and middle of each of the edges [48]. The octahedral sites can be seen in Figure 5.5, as the red, green, and white dots. The black dots in this image are where the atoms are located. There is a slight expansion in the (111) plane and a contraction in the (200) plane. In order for the spacing between the (220) planes to be spaced equally, the line connecting the y and x intercepts would have to be the same length as the normal crystal. Since the distance between the (200) planes is increasing, there is growth along the x-axis of the crystal. In order to keep the line connecting the x and y intercepts the same, there has to be contraction along the y-axis. Since the (220) plane gave the accepted value for FCC crystals and there is not more of a distortion between the (111) planes, there is no growth along the z-axis. Therefore, the impurities occupy the edge sites along any edge parallel to the x-axis, indicated by the green colored sites.

5.4: Sodium Borohydride Reduced Synthesis

The iron nanoparticles produced using sodium borohydride were the smallest nanoparticles with the smallest size distribution created in this study. The 0.5 g/L iron concentration produce 4.81 nm particles, and when 3% copper is added to the solution, these sizes dropped to 3.86 nm averages, with standard deviations of 0.64 and 0.66 nm respectively. While anionic surfactant was added to the mixture, which would help keep the particles small, the sodium borohydride will
deposit some boron into the nanoparticles. The boron will form iron boride, causing the creation of defect sites inside the nanoparticles. It is possible that the boron sits inside the tetrahedral or octahedral sites inside the iron. When copper is added to the same mixture, this creates more defects, causing the particles to be smaller when they are grown. If the approximate iron to boron ratio is 4:1, as the literature reports, the iron to copper ratio is closer to 33:1. However, because copper is so much larger than boron, it will put much more strain on the iron lattice, which might account for the nanometer sized drop in diameter.

5.5: Nanotube Synthesis

Carbon nanotube forests were produced with the 0.5g/L iron catalysts prepared in methanol reduced by sodium borohydride. While there was slight nanotube growth in the similarly produced nanoparticles produced in ethanol. This suggests that boron in the nanoparticles hinders the growth of carbon nanotubes. Carbon nanotubes were also produced using the polyphenol coated iron nanoparticles in a chemical vapor deposition system. The nanotubes were produced at a fast enough rate that they were able to form a continuous stream of nanotubes, which were able to be collected. In both cases, these nanoparticles have shown catalytic capabilities for growing nanotubes.

5.6 Error Analysis

Both of the axes of the histograms in Chapter 4 have inherent error. The main source of error in the x-axis of each of the histograms is the rounding error of 0.5nm. There is also error inherent in measuring the nanoparticle from the images, where each pixel is roughly equal to
0.28 nm, combining to a potential error of 0.78 nm. The only image that has a different x-error is the histogram for the iron sodium borohydride nanoparticles in Figure 4.28. Each pixel is worth 0.35 nm, making the error 0.85 nm in the x-direction. They error in the y-axis is related to the x-axis. If we assume that the nanoparticles form following a Poisson distribution, the error of the average diameters can be found by calculating the standard deviation of the nanoparticles and applying the following formula

$$\varepsilon = \frac{\sigma}{\sqrt{n}}$$  \hspace{1cm} (5.3)

Where “$\varepsilon$” is the error, “$\sigma$” is the standard deviation, and “$n$” is the number of samples, which is always 50 for the histograms.

Neither of these errors take into account the shape of the nanoparticles. By convention, nanoparticles are measured by their diameter, assuming a cross sectional perfect circle. Many of the nanoparticles that are seen in this study are not circular, but are rather, ellipsoidal, rectangular, or triangular. If the nanoparticles were too different in shape (e.g. rod like, or triangular), the nanoparticle was ignored in the average diameter measurements. Nanoparticles that were hard to distinguish from their neighbors were also neglected. For the less egregious shapes (e.g. slight oval, rounded square) the nanoparticles were taken into the diameter measurements and fitted to a circle. These nanoparticles were measured to minimize the area of the fitted circle filled by the background of the image.
Chapter 6: Conclusions

The goal of this work was to study the synthesis of iron nanoparticles and the factors that play a role in the size selection and shape of the particles. First we looked at the thermal decomposition of iron nitrate in an inert environment with hexadecylamine. As the iron nitrate boiled and decomposed it was mixed with the hexadecylamine making particles of an average diameter of 6.45 nm.

Next, we looked at a polyphenol reduction process using polyphenols from green tea and polyphenon-60. The first set of experiments was done to show how the change in temperature and polyphenol source changed the size of the nanoparticles. As the temperature increased, the nanoparticles became smaller, from 15.78 nm to 13.20 nm, but the standard deviation began to grow from 3.60 nm to 3.72 nm. Additionally, the morphology of the nanoparticles grown at 0 °C were slightly different, with more rod and oval-like shapes, than those grown at higher temperatures. The polyphenol source also plays a role in their size, where those made with extracts from Bigalow Green tea, were significantly larger than those produced by Chinese Green Tea. This may be due to different chemistries due to the different types of polyphenols which could reduce the iron.

We then looked at the concentration of iron and polyphenols and how they affect the size of the nanoparticles. We found that the nanoparticles shrunk in size between 0.1 to 0.5 g/L iron concentrations with 0.94 g/L polyphenols, from 5.95 nm to 5.76 nm along with a decrease in the standard deviation from 1.83 to 1.23 nm. This most likely occurs because of local concentration depletion as the nanoparticles grow. There is a large increase in size and distribution of the nanoparticles from the 0.5 to the 2.5 g/L iron concentrations from 5.76 nm to 16.27 nm. This is suspected to be due to a great increase in iron content, as well as the depletion of the polyphenols.
When the polyphenol concentration was increased to 1.5 g/L, the 2.5 g/L iron sample decreased in size from 16.27 nm to 7.37 nm with a similar decrease in size distribution from 2.83 nm to 1.44 nm. This further is evidence that the polyphenol concentration acts as a capping agent for the nanoparticles. The 0.5 g/L sample grew in both size and distribution from 5.76 nm to 8.46 nm in diameter and 1.23 nm to 2.90 nm in standard deviation.

X-ray diffraction was run on the polyphenol reduced samples to confirm the presence and phase of the iron. The x-ray spectra showed that iron was present, but it was in a distorted FCC phase. Due to the presence of carbon from the polyphenols, it is likely that the FCC was distorted due to carbon impurities. The lattice distortion resulted in a growth of crystal in the x-direction, shrunk in the y-direction, and remained constant in the z-direction suggesting that the impurities are on the octahedral sites of the iron crystals, on any edge that was parallel to the x-axis. When the sample is annealed at 250 °C, small peaks of BCC iron began to appear as well as some iron oxide. The fact that iron oxide did not appear on the sample previous to the annealing, means that the iron is most likely coated by the polyphenols, isolating it from oxygen from the environment. This allows them to have some air stability.

The polyphenol coated nanoparticles that were seen were typically in icosahedral or decahedral shapes. These shapes, most often found in FCC nanoparticles, are the result of crystal twinning which occurs at room temperature. The presence of these twins and the FCC phase for iron means that these nanoparticles are at a very high pressure.

The synthesis process using sodium borohydride and ferrous chloride with an anionic surfactant produced the smallest nanoparticles with a size of 4.81 nm and standard deviation of 0.64 nm. However, these nanoparticles seem to agglomerate probably due to magnetic forces. This limits the potential use of these nanoparticles. However, these nanoparticles, when produced in
methanol, have been shown to grow carbon nanotube forests. When 3 iron weight percent copper was added to the solution the nanoparticles, shrunk to 3.86 with a standard deviation of 0.66 nm. In summary, the results of this study are: (1) we have successfully made iron nanoparticles in the right size range, (2) the nanoparticles have a small distribution, (3) we can grow nanotubes from these catalysts in CVD systems, (4) the internal pressure of the nanoparticles is high, (5) the iron nanoparticles are in a FCC phase, (6) there appears to be carbon occupying some of the octahedral sites inside the iron, (7) room temperature twinning inside the iron nanoparticles occurs, (8) the nanoparticles are in icosahedral and decahedral structures, (9) the iron nanoparticle that are coated in polyphenols are air stable, (10) adding copper to the nanoparticles makes them smaller.
Chapter 7: Future Work

Nanoparticulate iron has multifunctional properties. This thesis however was designed to focus on the use of iron nanoparticles as catalysts and some of the basic structure. The following questions remain of interest in determining the values and characteristics of the nanoparticles.

1. What is the melting point of the nanoparticles? As the nanoparticles get smaller, there is a higher surface to volume ratio of atoms. Since melting initially starts on the surface, melting point depression of nanoparticles can be observed.

2. What are the different polyphenol chemistries, and their efficiencies, that lead to iron nanoparticles? With there being so many kinds of polyphenols, there may be more than one way to reduce iron to a nanoparticle state. If the size depends on the chemistry, then it may be possible to make a very narrow particle distribution, with little loss to other competing chemical reactions.

3. What are the magnetic properties of the nanoparticles? While FCC iron is not ferromagnetic in bulk form, FCC nanoparticles may be ferromagnetic, or superparamagnetic, where the magnetization of the nanoparticles can randomly flip due to the temperature.

4. What are the optical properties of the nanoparticles? Due to their small size, and quantum nature, the nanoparticles should have discrete absorption patterns. Additionally, the complex index of refraction and Brewster angle should differ from the classical case for iron.

5. How do these nanoparticles sinter? Sintering is the compacting of many smaller particles to form one large mass by thermal or pressure effects without melting. Due to their small size, these nanoparticles are more likely to fuse to reduce the total energy of the system.

6. How can these nanoparticles be used for biomedical applications? With the advent of pure iron nanoparticles, it is possible that these nanoparticles can be used to produce medicine for cancer
and other ailments. If the iron can be bonded to various chemicals, and stored in polyphenol solution, which is fairly innocuous, then it could provide a method for the storage and production of these particles.
List of References


[13] “Particle in a 1-Dimensional Box.” UC Davis Chemwiki. <http://chemwiki.ucdavis.edu/Physical_Chemistry/Quantum_Mechanics/05.5%3A_Particle_in_Boxes/Particle_in_a_1-dimensional_box>
Synthesis and Characterization of Iron Nanoparticles


<http://chemwiki.ucdavis.edu/Analytical_Chemistry/Electrochemistry/Redox_Chemistry/Oxidizing_and_Reducing_Agents>
Synthesis and Characterization of Iron Nanoparticles


[38] Fenton, Thomas. Private communication.


<http://newton.umsl.edu/run//nano/jmoltesc.html>


<http://www.tf.unikiel.de/matwis/amat/def_en/kap_1/illustr/t1_3_3.html>