THE DEVELOPMENT AND STUDY OF A NOVEL SYNTHESIS FOR PHOSPHINE STABILIZED GOLD NANOPARTICLES

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Larger scale synthetic methods are needed if nanoparticles are to become important building blocks for the production of a wide range of technologically useful materials. This thesis describes the development of a new biphasic synthesis for triphenylphosphine stabilized gold nanoparticles that safely and easily produces gram quantities of nanoparticle material.

The properties of ligand stabilized gold nanoparticles techniques used to characterize them are described for the lay reader, emphasizing connections with modern life. Through these descriptions, it is hoped that the reader will understand the motivation for research on nanometer scale materials and how chemists are attempting to meet the technological challenges posed by such materials.

The new synthesis presents opportunities for research on phosphine stabilized gold nanoparticles that were not available using traditional synthetic routes. These

include alternative phosphine ligands and rational size control of the gold core. Such possibilities and preliminary results are presented for the future work which has been permitted through the success of the new synthesis.

ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

Motivations for Chemical Research on the Nanometer Scale

Chemists traditionally study the very small. From Lewis dot structures in the early 20th century to Linus Pauling's hybrid orbitals in the mid-20th century to current computer-based molecular modeling algorithms, chemists attempt to describe the world at a molecular level. In the study of materials, chemists study molecules that lie between the realm of the atomic physicists and the macroscopic engineers, positioning it somewhat awkwardly in the minds of many in the so-called "hard sciences." This recently has been changing, with chemists and chemical approaches expanding into non-traditional fields. Theoretical nuclear chemists are now commonplace, and many larger systems have come under scrutiny by chemists. Some of the more famous examples include studies on relatively large molecules such as proteins, or more recently, large carbon networks such as Buckyballs [*1*] and carbon nanotubes [*2*]. (Figure 1.1) Such research has extended the realm of chemistry beyond individual molecules to

macromolecules and extended assemblies. This has allowed chemists to help in the development of nanoscale technologies.

Figure 1.1. The Buckminsterfullerene C_{60}. Also known as the Buckyball.

While chemists have begun studying larger systems, the electrical engineering profession has been hard at work designing smaller systems to meet the increasing demands placed upon modern devices, particularly in the design and manufacture of computer chips in the semiconductor industry. For the last twenty years, the semiconductor industry has been miniaturizing their chips using technical improvements on the technique of lithography. Lithography, which uses light to "etch" the circuits into the silicon wafer, has a fundamental lower size limit on the order of the wavelength of light used (visible light is ~400nm to ~725nm) Although this limitation has been lowered by the use of lower wavelength light and circumvented with mechanical tricks, devices made using lithography will soon reach a fundamental lower size limit due to quantum size effects.

Quantum size effects are only observed in systems which are extremely small. At these small sizes and masses, matter no longer behaves in the classical manner, that is like particles, but instead behave more like waves (this is known as the wave-particle duality). This results in the peculiar observation that when the "wires" on the chip become too closely spaced, the electrons in them no longer recognize the gaps between them as barriers to their movement, allowing them to travel freely through the barriers in a process called electron tunneling. As a result, conventional techniques will soon become limited by the barrier limit for electron tunneling, as control of current flow in circuits containing gaps smaller than the limit is not possible. This leaves room for the creation of new techniques and materials for devices that rely upon tunneling to function. This problem has been vexing to the traditional electrical engineers, who are not experienced with materials of this size. It is chemists, who study molecules on the size scales required for such devices, are beginning to answer this challenge for new materials. One such material is the ligand stabilized nanoparticle.

Description of Ligand Stabilized Nanoparticles

In order to follow the chemistry described in this thesis, the reader needs to understand what ligand stabilized nanoparticles are. While some aspects of nanoparticle research can be a little confusing even to the experienced chemist, a basic understanding of nanoparticles is not difficult.

The primary descriptor of nanoparticles is their size. A nanoparticle can be described as a ball with a diameter of anywhere from around 1 nanometer (nm) to upwards of 50 nm.[1] In the Hutchison group, we typically work with nanoparticles between 1 and 10 nm, as this size range possesses many of the exciting properties necessary for new materials on the nanoscale. It is important to note that few nanoparticle preparations create a single molecular species (like the bucky ball, for instance). Because of this, they are best described by an average size and a dispersity, or the amount that the nanoparticles statistically deviate from the average size.

The nanoparticles that are made in the Hutchison lab can be described as a combination of two regions, the metallic core and the stabilizing substance that surrounds it, called a ligand shell. This is seen in the following figure. (Figure 1.2)

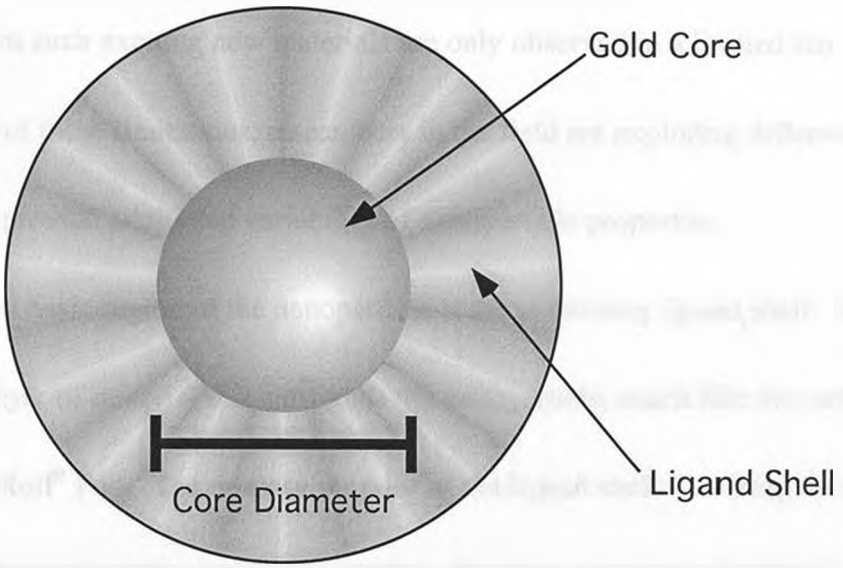

Figure 1.2. A cartoon of a ligand stabilized gold nanoparticle, emphasizing important characteristics described in the text.

The core, which is often metallic, gives nanoparticles many of their potentially useful properties. These properties, such as their interactions with light (their color or fluorescence) or electrons (their electrical properties), are highly dependent upon both the composition and size of the core. By using different materials, such as semiconductors (cadmium sulfide or cadmium sellenide) or conductors (gold, silver, platinum), scientists are able to experiment with new materials to take advantage of such optical and electrical effects. In addition scientists often take advantage of size dependent properties, an example being a color change when gold nanoparticles reach a certain size.[2] While impressive, control of nanoparticle composition and size is limited. Variation in core composition is restricted by the periodic table, as only a few elements have been found to

be suitable building blocks for nanoparticle synthesis. Also, the unique properties that make nanoparticles such exciting new materials are only observed in a limited size regime. Because of these limitations, researchers in the field are exploring different ligand shells that provide additional variability of nanoparticle properties.

The second basic region of the nanoparticle is the stabilizing ligand shell. The ligand shell is a layer of material that surrounds the nanoparticle, much like the candy shell of a TootsieRoll® Pop. The primary purpose of the ligand shell is to keep the core regions from coming into contact with one another. Because of their small size, the core regions are in a higher energy state than they would be in a bulk material, meaning that they prefer to be with a larger number of like atoms. If the cores are allowed to come into contact they fuse into larger and larger particles until this lower energy bulk state is achieved (often seen on the glassware we use when handling nanoparticles as a pretty golden coating).

While adding stability is by far the most important aspect of the ligand shell, the most interesting aspect of this layer is the control it has over nanoparticle properties. Because the ligand shell directly interacts with its surroundings, controlling this layer allows for the manipulation of these interactions. Nanoparticles can interact with their environment in a number of ways (Figure 1.3)

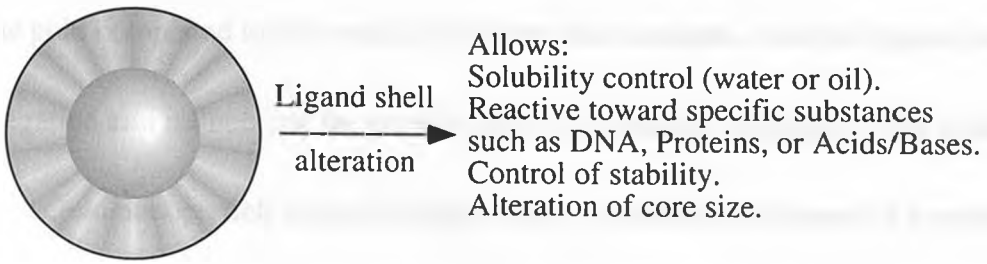

Figure 1.3. Altering the ligand shell can change many nanoparticle properties.

Foremost on this list is the ability of the ligand shell to make the nanoparticle soluble. By using ligands that are soluble in different liquids, we can make nanoparticles that are soluble in water, or nanoparticles that are soluble in organic solvents like oils. The solubility of the nanoparticles allows the use of solution phase molecular chemistry on them. [*3*] The ligand shell can also control how nanoparticles interact with other, larger, substances. For instance, nanoparticles can be made that bind DNA, proteins, or any other surface merely by controlling the nature of the ligand shell.

A Brief Background on the Synthesis of Ligand Stabilized Gold Nanoparticles

The synthesis of nanoparticles is obviously a requirement for their use and study. Currently, two techniques are widely used to synthesize sub 12 nm ligand stabilized gold nanoparticles. These syntheses involve the addition of a reductant (electron donor) to a

molecular gold species in the presence of the stabilizing ligand of choice. The reduction of the gold compound to the metallic gold core then proceeds, with the ligand preventing aggregation and influencing the growth rate of the resulting nanometer scale gold cores.

Gold nanoparticle research largely began with the development of a synthesis for triphenylphosphine stabilized gold nanoparticles by Schmid. [*4*] This synthesis produces a triphenylphosphine stabilized nanoparticle using a complicated, air-free setup that utilizes diborane gas as the reducing agent. Diborane is an extremely toxic, reactive, and flammable gas (it autoignites at 38°C). The caution needed when working with diborane gas makes the synthesis time consuming, stressful, and dangerous to the worker. Despite these "flaws" this method has been widely used because the final nanoparticle products are high quality, that is, having a small size with low dispersity (1.4 nm ± 0.4 nm). [*5*]

The synthetic technique for sub-10 nm gold nanoparticles that is more commonly used today is based upon the method of Brust. [*6*] This synthesis produces thiol-stabilized nanoparticles using the water soluble reducing agent sodium borohydride. This is a much milder and safer reaction than the Schmid route, but the nanoparticles made are slightly larger and in general have a wider dispersity. [*7*]

There are some distinct advantages and disadvantages to both routes. The Schmid route has two primary advantages in that it creates a high quality nanoparticles while providing a reactive ligand shell for further functionalization. These advantages are tempered by the dangers of diborane, the propensity of the phosphine nanoparticles to

decompose, and the reaction's low yield. In Brust type reactions the relative safety and ease of synthesis are its primary advantages. However, the final nanoparticles are typically lower in quality than the Schmid nanoparticles and are thiol-stabilized and unavailable for extensive ligand exchange reactions.

Ligand Exchange Reactions

To control reactivity, and to provide for control of the ligand shell, the Hutchison lab developed ligand exchange chemistry of the so-called Schmid particles. [*8*] (Figure 1.4) Briefly, we replace the existing ligand shell of a nanoparticle with a new ligand that binds better to the gold core. This is simply done in our system due to the relatively weak phosphine-gold bond on these nanoparticles, allowing their displacement by more stable ligands, such as thiols and amines. [*9*] The end result is a nanoparticle that is both more stable and with a controlled ligand shell through selection of the displacing ligand. Thus, we can control the properties of the resulting nanoparticles by simply deciding which ligand we exchange.

This route allows us to synthesize nanoparticles that have the same stability as the Brust route, but also retain the small size and dispersity of the Schmid route. We are also able to make a wide range of nanoparticles from a single intermediate nanoparticle.

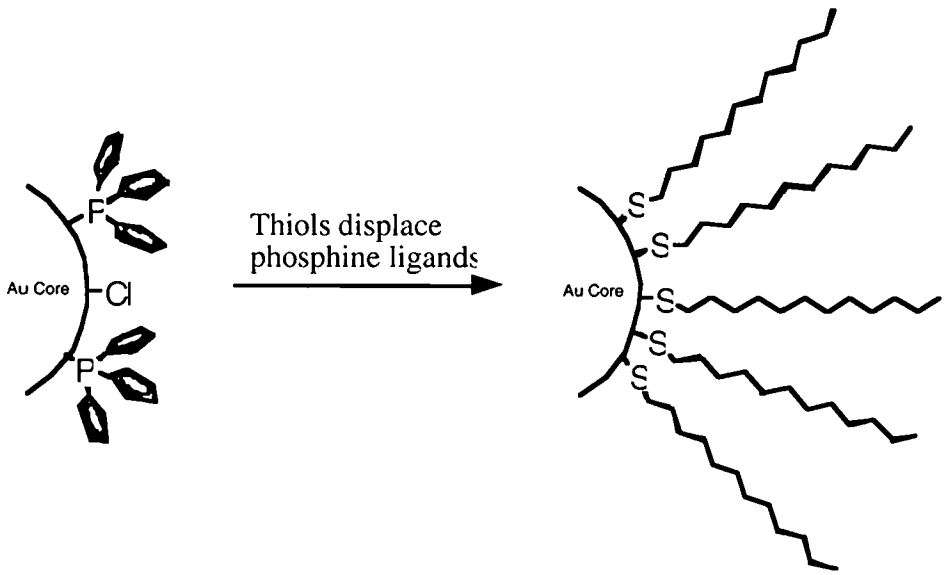

Figure 1.4. By replacing the relatively unstable phosphine ligand with a relatively stable thiol ligand, we are able to both stabilize and functionalize gold nanoparticles.

Nanoparticle Applications: Past, Present, and Future

By exploring the properties of varied ligand shells and metallic cores, scientists have devised a number of applications for nanoparticle materials. A sampling of such applications includes the use of nanoparticles as biological tags, in nanosensors and nanoelectronics, and as templates for other assemblies, such as protein crystals. However, the prohibitively expensive costs of nanoparticles inhibit their general use.

Use of gold particles as biological tags, especially in electron microscopy, has been commonplace for some time. However, the use of 1-2 nm nanoparticles for this purpose is relatively new and expensive. One company, Nanoprobes, Inc., offers gold

nanoparticles as tagging agents for a minimum price of $135 for 30 nanomoles (or ~0.5 mg). This is the primary company for the distribution of these nanoparticles in biological uses, and their prices reflect the high production costs that inhibit the growth of such technologies.

Nanoparticles have been investigated as nanosensors, relying in large part upon the optical properties of nanoparticles. Under certain conditions, nanoparticle aggregates can be detected by observing color changes of the solution. Mirkin et al. [*10*] exploits this property by controlling when the nanoparticles aggregate. In his system, the nanoparticles only aggregate and change color in the presence of the substance he wants to detect, which is DNA. One can envision using the aggregation properties of nanoparticles to detect a wide range of substances in easily monitored reactions, as the only equipment needed to detect the aggregates is the naked eye.

Nanoelectronic applications may rely upon electron tunneling between nanoparticles in arrays. Our lab, in collaboration with the Wybourne group at Dartmouth College, has pioneered the study of nanoparticles in these applications, being the first to observe Coulomb blockade at room temperature. [*11*] Coulomb blockade is the opposition to electron tunneling due to the opposing force of electrostatic repulsion. This opposing force is created by the electrons on the nanoparticle producing electric field that repels new electrons from hopping onto the nanoparticle, similar to when two magnets with like poles repel. This repulsion is eventually overcome by creating a driving force

that overwhelms this repulsion with high voltages, and current then flows. This property could be used to make such devices as transistors on a nanometer scale, well beneath the 100 nm "barrier" of current techniques. While it is still a long way from fruition, these possibilities drive much of the research in our lab.

Another possible application is in the use of nanoparticles as templates for protein crystallization. By organizing our nanoparticles into well-ordered arrays, we hope that the presentation of regularly positioned protein binding ligand will allow the growth of protein crystals underneath the nanoparticles. This idea is still in the realm of thought, but this possible biological application shows the far-flung utility of nanoparticles and nanoparticle based materials.

To accomplish all of these nanoparticle applications, existing methods of synthesizing nanoparticles need to be enhanced. As discussed earlier, both the Brust and Schmid syntheses have their advantages and disadvantages that make them only useful in certain situations. This thesis contains investigations into a novel synthesis of phosphine stabilized gold nanoparticles that will hopefully negate some of the disadvantages of both routes, retain the advantages, and extend the chemistry of these materials to previously unexplored areas.

CHAPTER II

CHARACTERIZATION TECHNIQUES FOR LIGAND-STABILIZED METAL NANOPARTICLES

Introduction

Chemists rely upon many characterization techniques to understand the compounds that they synthesize. Characterization can rely upon easily observable properties of the material, or it can rely upon sophisticated technology to describe materials in ways not accessible using our senses. Observable properties include color, shape, melting or boiling point, smell, and, many years ago, taste. While these are informative, it is difficult to extract molecular structure from such observations. Insight into molecular structure is obtained by many techniques, and all have become tools for chemical research.

Unlike simpler compounds, nanoparticles require many characterization techniques to answer the many questions about their structure. This is mostly due to their

distinct metallic core and stabilizing ligand shell. These highly different layers necessitate the use of multiple techniques to fully describe their structural properties. Size dispersity also complicates their characterization. When we think about the core, we would like to probe the primary descriptors of size and dispersity, as well as its shape and electronic properties. To understand the whole ensemble of nanoparticles, we need to know its average composition, that is, how much ligand and core material there is in each particle ensemble. To finish describing the nanoparticle, we would like to know the composition of the ligand shell and the ligand's interaction with the environment. This chapter describes some of the techniques used to answer such questions.

Description of Characterization Techniques

Direct Imaging by Transmission Electron Microscopy

While many techniques exist to measure the mean size of nanoparticles exist (such as powder x-ray diffraction and mass spectrometry), the Hutchison lab prefers to directly image nanoparticle material. Direct imaging allows for the simultaneous determination of both the size AND dispersity of the metal core, while using very little material. Typically, nanoparticle images are obtained using transmission electron

microscopy (TEM), but atomic force microscopy (AFM) is occasionally used as well. I will only discuss TEM here.

Transmission electron microscopy is a technique commonly used by scientists to image the very small. This technique is very similar to light microscopy, but instead of light beams focused by glass lenses it utilizes an electron beam focused by electromagnetic "lenses" under high vacuum. (Fig 2.1)

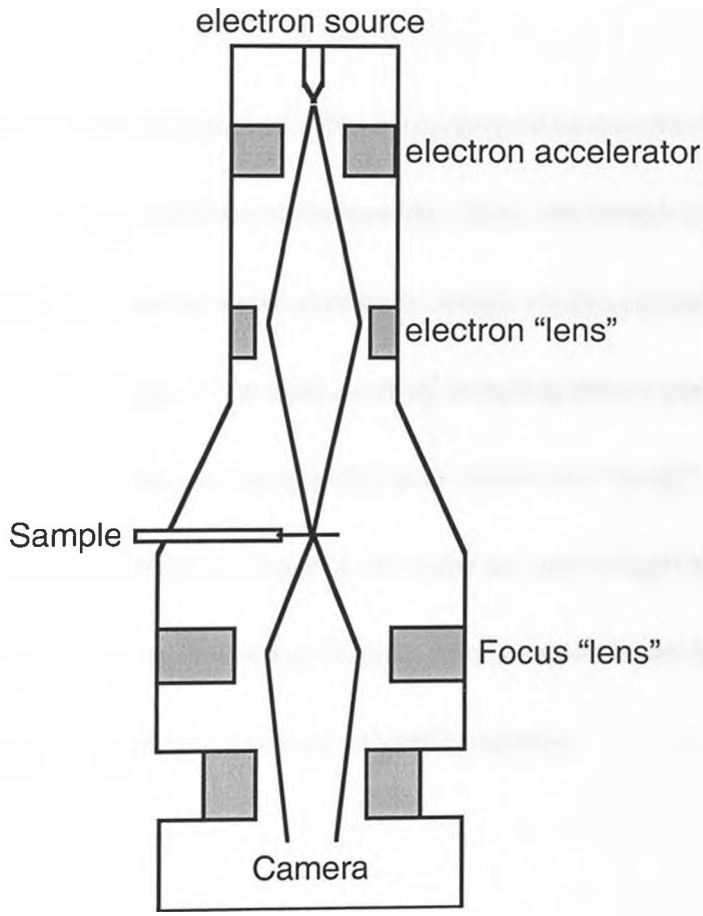

Figure 2.1. Diagram of a Transmission Electron Microscope. Notice that the electron beam is centered on the sample by electromagnetic lenses.

To be observable by electron microscopy, a material needs to be have regions that are opaque to the electrons passing through them. Nanoparticles are ideal candidates for TEM, as the heavy gold atoms efficiently deflect electrons while the ligand shells allow electrons to pass through unimpeded. The deflection creates contrast on the image, similar to how a spider on a window creates contrast by deflecting light. Because of this contrast we are able to directly image the nanoparticles and, with correct calibration, measure their sizes as well. This technique also allows us to examine the shape of the nanoparticles.

The primary disadvantage of a direct imaging technique like TEM is that it runs the risk of being unrepresentative of the sample. Since the sample consists of billions of nanoparticles, the thousand or so nanoparticles which we can conveniently image are an extremely small percentage of the total, making sampling error a possibility that cannot be ignored. To counter this, we need techniques which can "image" the entire sample at once. To gain a representative picture of the cores we turn to light spectroscopy, in particular the ultraviolet-visible range of light, to examine the size-dependent electronic properties of the nanoparticles in a representative manner.

Ultraviolet/Visible Spectroscopy

Ultraviolet and visible light can change the electronic energy state of most molecules. This happens when light is absorbed by the molecule, changing the color of light that passes through the material (the transmitted light). This is why plate-glass windows have their spectacular colors, molecules in the glass absorb particular colors of light and characteristically change the color of the transmitted light. This effect is used by scientists to examine the electronic structure of molecules and materials using a technique called ultraviolet/visible spectroscopy (UV/Vis). Obtaining a UV/Vis spectra is done by placing the sample of interest in a light beam that contains all wavelengths, and detecting the intensity of the light at each wavelength after it leaves the sample. (Fig 2.2) If the sample absorbs a particular wavelength, this is easily seen by the instrument as an increase in the absorbence of the material.

The primary reason to examine gold nanoparticles using this technique is to confirm the core size as obtained by TEM. The reason this works is that when the nanoparticle core is above 2 nm, an absorbence appears at ~ 520 nm. [*1*] By looking at this feature, we can be confident that few particles greater than 2 nm are present in the sample.

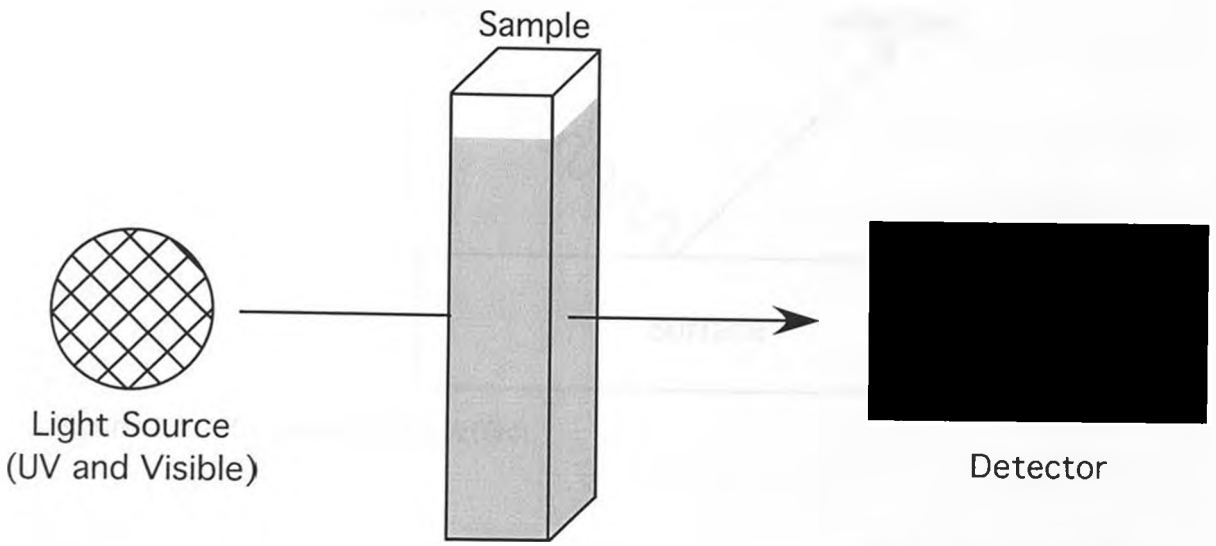

Figure 2.2. UV/Visible spectroscopy. The sample is dissolved in an appropriate solvent. The detector can be a sophisticated diode array or a simple photomultiplier device.

Elemental Analysis

The elemental composition of the nanoparticle is determined using the complementary techniques of x-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA). XPS is a technique based upon the photoelectric effect first explained by Einstein.[1] (Fig 2.3)

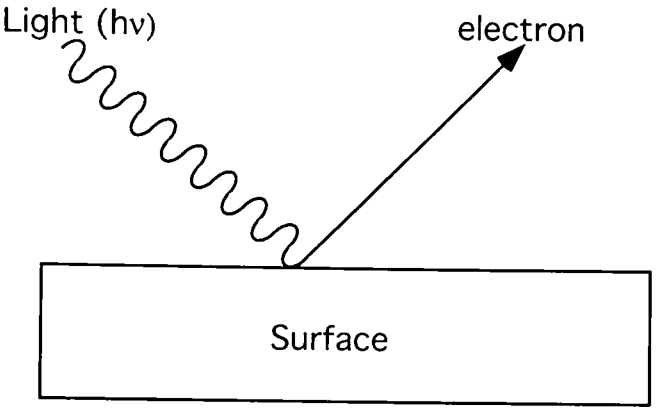

Figure 2.3. The photoelectric effect.

As its name implies, in XPS we bombard the sample with x-rays, which causes photoelectrons from the sample to be emitted. The emitted electrons have characteristic energies depending upon which element they were emitted from. Thus, by measuring the electron energy, we can determine which elements are in our sample and what state those elements are in. In addition, by counting the number of electrons emitted, the ratio of elements in the sample can be measured. This data is very useful in determining the elemental composition of our nanoparticles, but this technique is very sensitive to atmosphericimpurities such as the "fatty acid rain" that is floating through the air. Thus, it is beneficial to perform the experiments multiple times or have a second technique confirm any result.

As previously mentioned, a complementary technique to XPS is TGA . TGA is a simple technique that basically weighs the sample as it is heated. As the sample decomposes and the volatile components leave the sample, the mass drops. Common

airborne contaminants are volatile at lower temperatures than the nanoparticle ligand shell, allowing them to be disregarded in data work-up. As for nanoparticle components, only the ligand shell is volatile below 500° C, and therefore we can use this technique to measure the ligand to gold ratio in the sample, confirming the elemental data from XPS analysis.

Nuclear Magnetic Resonance

Among the most common technique used to analyze organic molecules is nuclear magnetic resonance (NMR). [2] This technique relies upon the interaction of magnetic moment of atoms such as hydrogen and phosphorus with an external magnetic field. Using radio waves to measure the strength of this interaction, chemists can extract the chemical environment surrounding the atoms of interest. This allows for structural information to be gained on molecules. This technique is also sensitive to subtle changes in the interaction of molecules, being able to discern properties such as molecular rotation or the interaction of molecules in solution. By using this technique, we are able to easily discern the composition of the ligand shell as well as the environment surrounding the atoms within the ligand shell. This also helps in determining the purity of the nanoparticles, as the amounts of unbound and bound ligand are easily monitored in NMR spectra.

Conclusions

This chapter has described several of the methods which are utilized to characterize ligand stabilized gold nanoparticles. This list is by no means exhaustive, but contains the techniques commonly used by the Hutchison lab to describe the nanoparticles that we synthesize. The following chapters contain descriptions of some of the work done by myself and others in the lab on a novel synthesis of phosphine stabilized gold nanoparticles. Chapter III contains the original synthesis, including information on the synthesis, purification, and characterization of these nanoparticles. In Chapter IV, I discuss some of the future work made possible by this synthesis, particularly the rational control of nanoparticle core sizes.

CHAPTER III

A NOVEL SYNTHESIS FOR SUB 2 NANOMETER TRIPHENYLPHOSPHINE STABILIZED GOLD NANOPARTICLES

Introduction

Phosphine stabilized gold nanoparticles are among the most widely studied of ligand stabilized nanoparticles. First described by Schmid *et al* in 1981,[*1*] the "Au_{55}" synthesis paved the way for theoretical and practical investigations of nanoparticle properties. [2] While recent nanoparticle research has focused on thiol stabilized nanoparticles due their ease of preparation and high stability,[*3*] the small size and low dispersity (1.4 nm ± 0.4 nm) [*4*] of triphenylphosphine passivated gold nanoparticles continues to make them important research materials. [*5*] Recent advances demonstrating the ability to exchange thiol ligands onto triphenylphosphine passivated nanoparticles have enabled the coupling of this small size with the stability of thiol-passivated gold nanoparticles. [*6*] This has allowed investigation of nanoparticle applications that require

both high stability and small core size, such as nanoelectronic phenomena like room temperature Coulomb blockade. [7] This chapter reports a convenient, scalable synthesis for ~1.4 nm triphenylphosphine stabilized nanoparticles that are comparable in both size and reactivity to the Schmid nanoparticles while utilizing a less hazardous reducing agent. In addition, the generality of this synthesis is shown through the successful synthesis of previously unknown aliphatic phosphine stabilized gold nanoparticles.

Synthetic Description

This synthesis is a one-pot biphasic reaction in which the nanoparticles can be synthesized and purified using simple techniques. (Fig 3.1) The phase transfer catalyst tetraoctyl ammonium bromide (1.60 g,2.92 mmol) and the gold source hydrogen tetrachloroaurate (1.00 g, 2.95 mmol) are first dissolved in a nitrogen sparged water/toluene biphasic solution (50 mL: 65 mL). Next, triphenylphosphine (2.32 g, 8.85 mmol) is added and the solution stirred for five minutes. Then, aqueous sodium borohydride (1.41g, 29.4 mmol, dissolved in 10 mL water) is rapidly added, upon which the solution immediately turns dark, with vigorous initial bubbling. This mixture is then stirred for three hours under nitrogen.

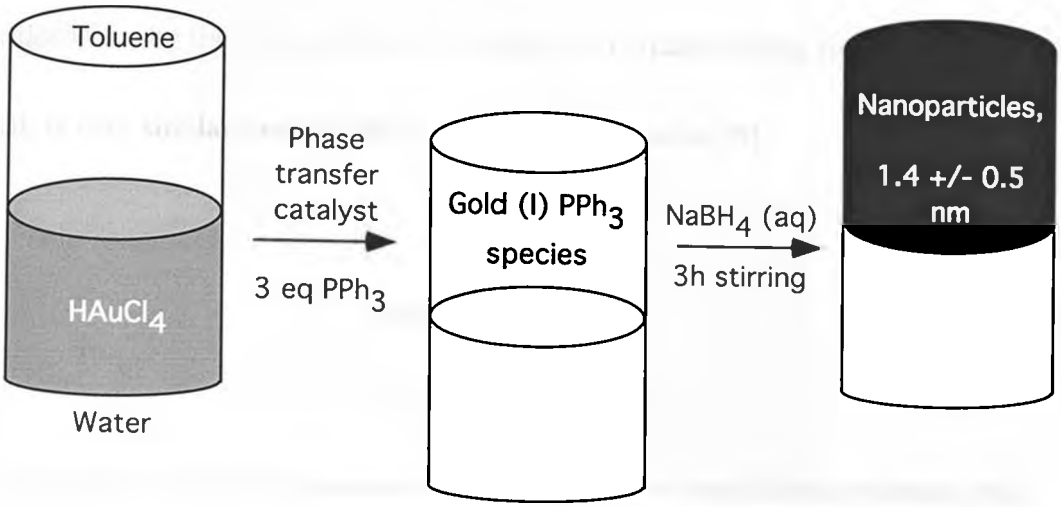

Figure 3.1. A pictographic scheme of the synthesis, emphasizing what is seen during the reaction.

The toluene layer is then separated from the aqueous phase and washed twice with 200 mL water. The toluene is then removed *in vacuo* with very little heat or with a stream of nitrogen. The resulting solid is then suspended in hexanes and placed on a glass frit. This solid is washed, alternating 100 mL of hexanes with 100 mL of a water:methanol solution (2:3), until approximately 500 mL of each has been used. It is then washed, with alternating 100 mL aliquots, with saturated sodium nitrite and hexanes for a total of 500 mL of each. This is followed by another 500 mL of the methanol:water solution, alternated with 50 mL aliquots of hexanes. Finally, we repeat the sodium nitrite and the methanol:water washes again, using 50 mL of hexanes between each 100 mL of aqueous washes. All of this is done primarily to remove the phase transfer catalyst, but it also removes triphenylphosphine oxide and triphenylphosphine from the reaction

mixture. The final product is obtained by two precipitations of the resulting black solid from chloroform by the slow addition of pentane. [*8*] The resulting yield, 120 mg of pure material, is very similar to the yield of the Schmid synthesis. [*8*]

Results and Analysis

In order to make comparisons with the products of the Schmid synthesis, the newly synthesized nanoparticles were analyzed to determined size and reactivity. Elemental analysis is awaiting final purification of the nanoparticles. Direct evidence of nanoparticle size and dispersity was provided by transmission electron microscopy (TEM). Samples synthesized in a similar manner to the above synthesis[2] were prepared by drop casting dilute methylene chloride solutions of nanoparticles onto carbon coated 400-mesh grids.[3] A representative TEM of these nanoparticles, (Fig 3.2) shows nearly monodisperse triphenylphosphine nanoparticles with a size of 1.4nm ± 0.5 nm.[4] This is in good agreement with the Schmid synthesis.

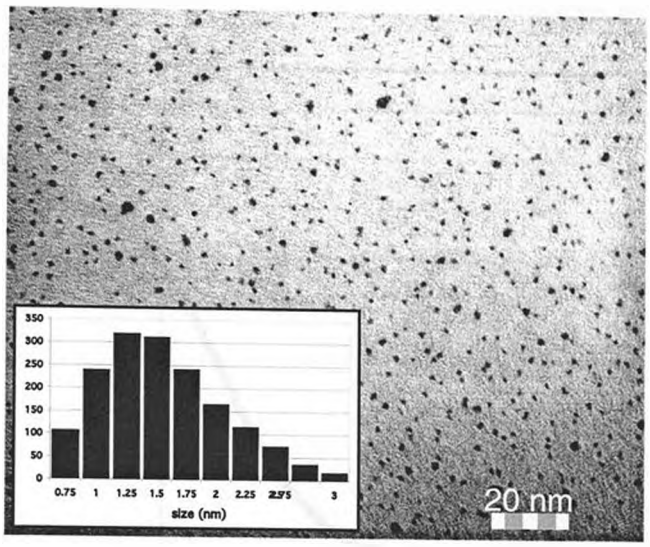

Figure 3.2. A representative TEM with corresponding size histogram showing the small size distribution.

While efforts were made to ensure that TEM images were representative of the bulk material, spectroscopic techniques that are truly representative of the bulk material, such as UV/Vis spectroscopy, must be used to confirm TEM size determinations. While nanoparticle UV/Vis spectra can be altered with changes in the passivating ligand, the absence of a significant surface plasmon resonance at ~520 nm is indicative of nanoparticles that are < 2 nm diameter. [9] UV/Vis spectra of newly synthesized nanoparticles are dominated by the interband transition, with no significant plasmon resonance. (Fig 3.3) This is consistent with our TEM results describing < 2 nm particles.

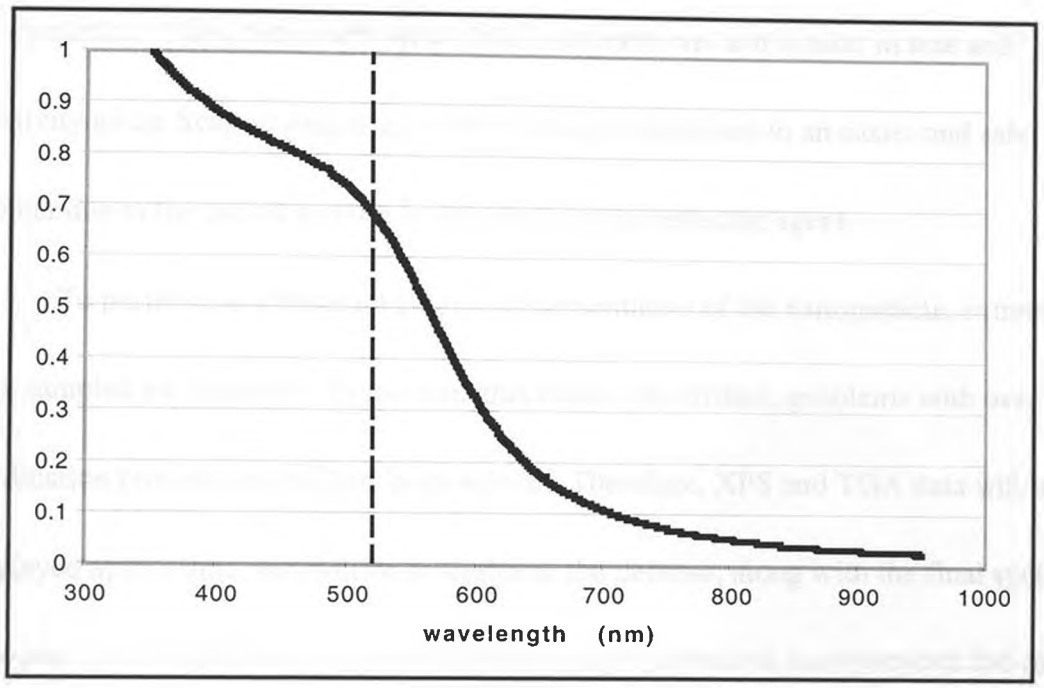

Figure 3.3. A typical UV/Vis spectra of small nanoparticles. Notice the broad, indistinct plasmon resonance at ~520 nm.

The reactivity of the newly synthesized nanoparticles to thiol ligand exchange was used to further confirm their similarity to other triphenylphosphine stabilized nanoparticles. Using methods previously reported, [*6*] we have successfully exchanged a wide variety of alkanethiol and other ω–functionalized thiol ligands, such as terminally charged thiol ligands that impart water solubility. [*10*] In each thiol for phosphine ligand exchange reaction, there is little change in the surface plasmon resonance of the UV/Vis spectra, indicating negligible size changes during the phosphine to thiol ligand exchange. [*6*] The success of the ligand exchange experiments indicate that the newly synthesized

nanoparticles have the proven reactivity of other triphenylphosphine stabilized gold nanoparticles. Thus, the newly synthesized nanoparticles are similar in size and reactivity to the Schmid preparation while being synthesized in an easier and safer manner due to the use of sodium borohydride as the reducing agent.

To perform an elemental analysis representative of the nanoparticle, extremely pure samples are required. At the time this thesis was written, problems with our purification procedures had just been solved. Therefore, XPS and TGA data will not be displayed at this time, but will be available at the defense, along with the final synthesis. However, the similarity in size between the newly synthesized nanoparticles and Schmid-type nanoparticles should allow us to directly compare atomic compositions. For direct comparison of our data with the Schmid nanoparticles, an average empirical formula can be generated assuming a core size of 55 gold atoms. Using preliminary data,[5] the average particle in our preparation is approximately $Au_{55}(PPh_3)_{12.5}Cl_3$, in comparison with the $Au_{55}(PPh_3)_{12}Cl_6$ reported by Schmid. As mentioned previously, this is preliminary and we will have more definitive description of the nanoparticle composition at the defense.

While we have shown this synthesis to have utility as a convenient, high yield synthesis of triphenylphosphine stabilized nanoparticles, we have also discovered that the new synthetic route can be applied to synthesize a wide range of phosphine stabilized nanoparticles. Substitution of PR_3 for PPh_3, and slight modification of the work-up, allows for isolation of alkyl stabilized nanoparticles in good yield. We have successfully

synthesized trioctylphosphine and tricyclohexylphosphine stabilized gold nanoparticles, (Fig 3.4) expanding the utility of the synthesis. To our knowledge, this approach is the first reported synthesis of alkyl phosphine stabilized gold nanoparticles.

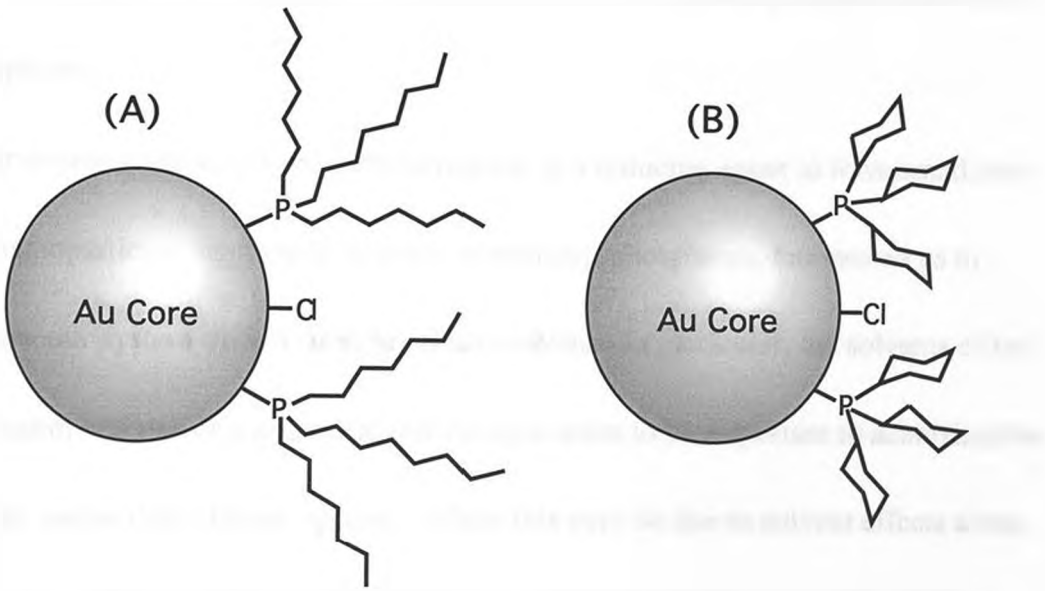

Figure 3.4. A cartoon of (A) tri-n-octylphosphine and (B) tricyclohexylphosphine stabilized gold nanoparticles.

Discussion

According to literature, this synthesis should not have produced nanoparticles of this size, with this dispersity. Instead, it should have produced smaller, cluster species. It has previously been accepted that borohydride reduction of gold salts results in smaller, molecular cluster species such as undecagold (Au_{11}). [*11*] The conditions of the previous syntheses involving sodium borohydride are: absolute ethanol using the gold (I) salt

precursor alone with no additional phosphine. In addition, Schmid's initial papers [*8*] suggest that triphenylphosphine is somehow necessary for the formation of small particles due to the relatively weak gold-phosphine bond in this system compared to other tri-substituted phosphines because of the weak basicity of triphenylphosphine relative to other phosphines.

Our demonstration of sodium borohydride as a reducing agent to form small, low dispersity nanoparticles, applicable to many substituted phosphines, has caused us to evaluate how our system differs from previous systems. In particular, the solvents of the biphasic system and use of a phase transfer catalyst seem to be important in achieving the nanoparticle, rather than cluster, species. While this may be due to solvent effects alone, i.e. a less polar solvent results in larger particles, the field must reevaluate the synthetic literature in light of this new synthesis. Also, the use of trialkyl phosphines shows that it may not be the weak basicity of triphenylphosphine that is special for small nanoparticle formation, but instead is another as yet uninvestigated property that causes the results Schmid reports.

Conclusions

The simplicity of this synthesis presents a unique opportunity for the expansion of phosphine stabilized nanoparticle research. The ability to easily and safely create relatively large amounts of quality nanoparticle material in a single step during a single

day will extend the accessibility of this compound to a wider range of researchers. In addition, this synthesis allows for flexibility in the synthesis of phosphine stabilized nanoparticles that is currently unknown. The highly flexible Brust synthesis of thiol stabilized gold nanoparticles has been exploited to control everything from the composition of the ligand shell to the core size of the nanoparticle. We have already shown that the new route allows for synthesis of the previously unknown alkyl phosphine stabilized gold nanoparticles. Variation of ligand to gold ratios in the Brust synthesis have been used to control the final size of thiol stabilized nanoparticle. [*11*] We anticipate that by utilizing similar techniques, we can achieve unprecedented size control of phosphine stabilized gold nanoparticles. This idea will be continued in the next chapter, where initial results suggest that altering the ligand to gold ratio will allow for the rational synthesis of size controlled triphenylphosphine stabilized gold nanoparticles.

CHAPTER IV

SIZE CONTROL OF TRIPHENYLPHOSPHINE STABILIZED NANOPARTICLES

Introduction

Nanoparticle core size has been shown to have significant control over the properties of ligand stabilized gold nanoparticles. In particular, optical spectra drastically change with differing core sizes, especially between 2 and 10 nm. [*1*] It is only recently that investigation began on methods to rationally control core sizes between 2 and 12 nm.[1] The primary reason for this is that syntheses of such materials are relatively new, and the mechanism of particle growth is not yet clearly understood. However, there has been work indicating that size control within this size realm is possible. The two primary means that this has been accomplished are through a ligand exchange growth mechanism or through manipulation of the direct Brust synthesis.

To my knowledge, the only size control of phosphine stabilized nanoparticles was not done directly on such particles, but through ligand exchange of triphenylphosphine

stabilized gold nanoparticles with primary amines. By exchanging the phosphine with pentadecylamine, it was found that the nanoparticles grew controllably to a size of ~5 nm. [2] It was also found that the amine stabilized nanoparticles could be further exchanged with thiols to make the more stable thiol stabilized nanoparticle. [3] However, this route was limited in that it would only result in a small range of larger core sizes, and a continuum of sizes could not be obtained.

Control of nanoparticle size by direct synthesis has been modeled using a nucleation-growth-passivation process in thiol stabilized gold nanoparticles. [4, 5, 6, 7] This has been examined primarily through the alteration of gold to thiol (gold to ligand) ratios in the initial reaction mixture. Using such methods, thiol stabilized gold clusters have been made with core sizes of 1.1 nm to 5.2 nm. [4, 5, 6] While impressive, such nanoparticles retain the disadvantages of the Brust synthesis, that is a higher dispersity and less reactive ligand shell than phosphine stabilized nanoparticles. Even though it has disadvantages, this system was studied for size control because of the ease of the synthesis. Because the new synthesis of phosphine stabilized gold nanoparticles is similar to the Brust synthesis, we are beginning to understand how to demonstrate the unprecedented size control of *triphenylphosphine* stabilized gold nanoparticles utilizing such methods. These experiments are described in this chapter.

Materials and Methods

All solvents and reactants were used as purchased. The synthesis is a biphasic reaction involving the sodium borohydride reduction of a gold tetrachloraurate triphenylphosphine solution. Gold tetrachloraurate (~0.1 g, 0.03 mmol) was dissolved in 5 mL of deionized water. The phase transfer catalyst tetraoctylammonium bromide (~0.15 g, 0.27 mmol) was then added, along with 5 mL of toluene. This solution was allowed to stir until the gold had been transferred into the toluene layer.

Two experiments were done, one to explore how the gold:phosphine ratio altered the size of the nanoparticles, and another to examine how the concentration of species changed the size of the synthesized nanoparticles. These will be referred to as experiment A and experiment B respectively. In experiment A, phosphine was added until gold:phosphine ratios of 0.2, 0.33. 0.96, 3.2, and 7.4 were obtained. As a control, an additional sample was done without added phosphine. In experiment B, the gold:phosphine ratio was kept at 0.33, but the amount of toluene was increased to 50 mL (resulting in 6 mM and 0.6 mM solutions). After the solutions were allowed to stir for approximately 5 minutes, sodium borohydride (~0.14 g 2.9 mmol) dissolved in 1 mL of water was quickly added. The solutions immediately turned dark, with vigorous bubbling. These were allowed to stir for one hour, at which time the toluene layer was separated and the solvent removed with a stream of nitrogen.

Results

The resulting material from all experiments was subjected to UV/Vis analysis.

Experiment A (Fig 4.1)

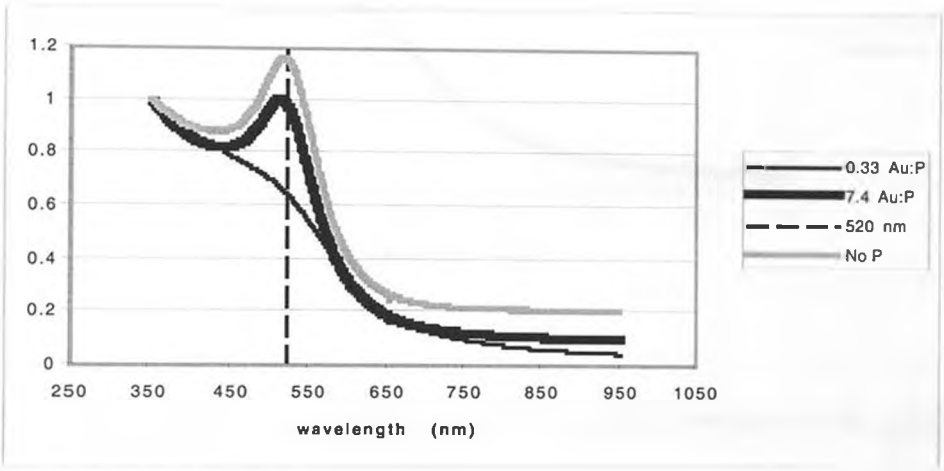

Figure 4.1. UV/Vis of a portion of experiment A, variation of gold to phosphine ratios.[2]

This result clearly shows that size control by variation of gold to ligand ratios is possible by decreasing the amount of phosphine in the reaction. Also, it shows that a limit is reached when no phosphine is present, presumably due to tetraoctylammonium bromide stabilization of the nanoparticle cores. However, it remains unclear what the controlling factors in this reaction are. Some possibilities will be discussed later.

In experiment B the samples were found to be nearly identical by UV/Vis. (Fig 4.2)

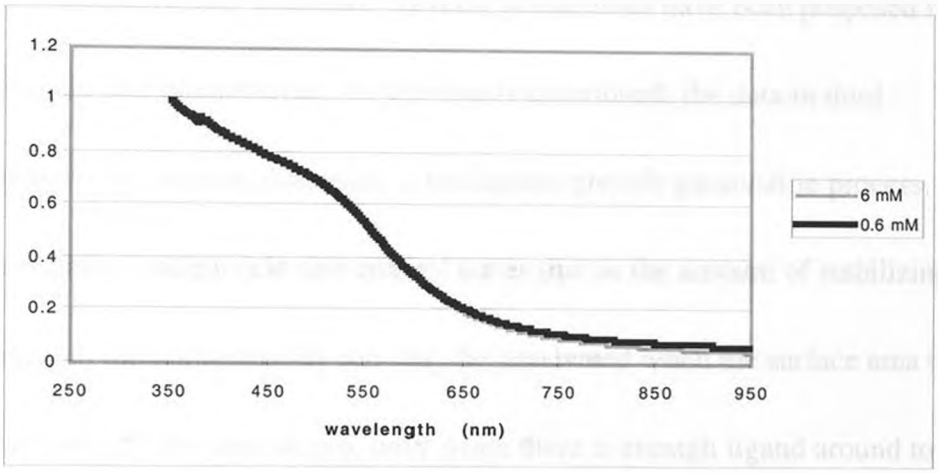

Figure 4.2. Altering $HAuCl_4$ concentration causes negligible changes in the optical properties of the nanoparticles.

This allows us to conclude that altering the concentration of gold species within these limits has little effect on the size of the resulting nanoparticles. Thus, we preliminarily conclude that small changes in concentration are negligible factors in nanoparticle size, important for the ease of our synthetic method as precise measurements of concentration are not needed to achieve reproducible results. To confirm this result, TEM could be performed on each sample. However, in this size realm, UV/Vis is a sensitive measure of core size.[3]

Discussion

The existence of rational size control in phosphine stabilized nanoparticles is a discovery that warrants further attention. Several possibilities have been proposed in literature to explain this phenomena. As previously mentioned, the data in thiol stabilized nanoparticles is consistent with a nucleation-growth-passivation process. One hypothesis to explain nanoparticle size control states that as the amount of stabilizing ligand is decreased, the nanoparticles can only be passivated when the surface area to volume ratio is low. [*5*] In other words, only when there is enough ligand around to cover the surface can nanoparticle growth be stopped. Also, the possibility exists that the core size is larger due to less gold (I) salt and more gold (III) salt in the intermediate steps, which may cause different growing processes to occur than in the case where only gold (I) is present.

Conclusions

Science is a work in progress, and most experiments lead to further avenues for exploration. This chapter describes some of the preliminary work that has been done to see if the rational size control of phosphine stabilized gold nanoparticles is possible. The results so far seem to suggest that such control is possible through variation of the ligand

to gold ratios. Many complications still exist. These include such questions as: Which is stabilizing the nanoparticles in the low phosphine cases, the phosphine or tetraoctylammonium bromide? Why does concentration seem to play little role in size control, as one might expect based upon a nucleation-growth model? or What is the dispersity of these larger nanoparticles? These questions remain unanswered, and stand waiting for the next discovery.

Endnotes

Chapter I

[1] For those unfamiliar with a nanometer, there are ten million nanometers in one centimeter ($1nm = 10^{-9}m$).

[2] Optical properties are also used to detect aggregates of particles, see Reference [*9*].

Chapter II

[1] Einstein won the Nobel prize in 1921 largely for this discovery.

Chapter III

[1] The synthesis is also successful with non-sparged solvents under air

[2] The nanoparticles in the images were synthesized utilizing one equivalent of phase transfer catalyst instead of the 0.3 equivalents noted in the chapter. The reason that we decreased the amount of phase transfer catalyst is that purification was shown to be difficult with higher amounts of phase transfer catalyst.

[3] Images were taken on a Phillips CM-12 electron microscope operating at 100 kV. Images were recorded on film, scanned as negatives, and size measured using NIH-Image, a shareware image processing program.

[4] A total of 1628 particles were examined from two separate synthetic runs (by two different researchers) were measured for the triphenylphosphine nanoparticles. We excluded background noise and obvious agglomerates from the measurements by removing core sizes of < 0.5 nm and > 3 nm from the analysis.

[5] XPS spectra gave mass ratios of 71% gold, 26% carbon, 2.6% phosphine, and 0.7% chlorine, corresponding to molar ratios of 18 Au : 108 C : 4.3 P : 1 Cl. TGA results indicating mass ratios of 71% gold to 29% ligand independently confirmed the XPS data.

Chapter IV

[1] Above 12 nm, well defined techniques exist for the synthesis and purification of nanoparticles that rely upon well developed colloid chemistry first developed by Farraday in 1857. (Farraday, M.; *Philos. Trans. R. Soc. London* **1857**, *147*, 145-181)

[2] UV/Vis spectra were normalized at 350 nm from similar nanoparticle concentrations.

[3] In recent work, we found that nanoparticles with similar UV/Vis spectra are ~2.6 nm in size, while smaller nanoparticles have an obviously different plasmon.

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