Synthesis and Characterization of Gold Nanoparticles

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Outline of thesis

This thesis is focused on the synthesis of three different shapes of gold nanoparticles; the gold nanosphere, the gold nanorod and the gold nanocube. These will be synthesized using wet chemistry methods and characterized using UV-Vis-NIR spectroscopy and dynamic light scattering. The results will be used to draw some conclusions as to what factors influence the growth of gold nanoparticles.

Chapter 1 Aims to provide a brief introduction of nanotechnology and its applications and introduces the ideas and methods used in the synthesis and characterization of gold nanoparticles in the thesis.

Chapter 2 Explains the physics behind the particular methods used in the thesis to synthesize and characterize gold nanoparticles.

Chapter 3 Explains the methodology of the experiments

Chapter 4 Reports the results of the experiments.

Chapter 5 Attempts to draw conclusions from the acquired data.

1 Introduction

Gold nanoparticles (AuNPs) have been used since ancient times to make stained glass, but it was long assumed that the color of the gold suspension was a result of the chemicals used to prepare it. In 1857 Michael Faraday produced the first pure sample of gold colloid and discovered that its color is due to the size of the gold particles.

Nowadays nanoparticles are extensively studied for the distinct properties that many materials exhibit on the nano-scale. The properties are most important to the AuNPs synthesized during this project are the plasmonic properties and the surface enhanced Raman-scattering (SERS) of the nanoparticles. The plasmonic properties of gold nanoparticles depend on the size and shape of the nanoparticles making the synthesis of specific sizes and shapes of nanoparticles an important area of research. Surface enhanced raman-scattering depends heavily on the local geometry of the nanoparticle.

The Plasmon is a quantum of surface-charge oscillation; the oscillation is started as a result of an external electric field forcing the surface charges on the particle to amass at one end. When the electric field disappears the resulting field will be opposite to the original, caused by the massing of charge. This vibration may then continue until the associated energy is dissipated through inter-electron clashes. The plasmonics of a material only appear on the nanoscale, because on larger scales the realignment of the surface charge to an external field is too quick for surface-charge oscillation to occur.[1]

Raman scattering is the inelastic scattering of a photon. This means that the outgoing photon has a wavenumber different from the incident photon. This can happen if the photon excites some quasi-particle in the material, such as a phonon or a plasmon. Usually the intensity of the Raman scattered light is very low, most light is scattered elastically, however there are techniques to amplify the effect. In metallic nanoparticles the origin of the Raman scattering is the excitation of the plasmon. For particles that are small compared to the wavelength of the incident light this leads to an enhancement of the intensity of the Raman-scattered light by
a factor of as much as $10^{11}$. This effect is strongly altered by the binding of a molecule to the surface of the particle, and this can be used to measure the presence of singular molecules.[2]

Au NPs have many applications in a wide variety of fields such as medicine, energy, electronics and optics. In medicine Au NPs are being researched for many applications including as contrast agents[3], drug delivery vectors[4], localized heat therapy[4], ultra-sensitive biomarkers[5] and more. As a contrast agent for CT-scanning Au NPs has shown better contrast properties than those currently in use because gold has a higher radio-density than the contrast agents used. Au NPs also have good qualities as a drug delivery vector; one reason is that multiple different functional groups may be attached to the same Au NP, allowing for targeted drug delivery. The high surface area to volume ratio makes nano-scale particles especially suitable for this task, also absorption of light by the plasmon of Au NPs can be used to initiate heat-sensitive release of medical compounds. The plasmonics of the Au NPs also allow for localized heat therapy by the absorption of light of specific wavelengths. The energy absorbed is later dissipated to the surrounding area. This technique has been shown to be highly efficient in conjunction with heat-sensitive release of anti-carcinogens as a method of fighting cancer tumors.

In energy technology Au NPs have been studied as a means of improving the efficiency of solar panels[6], their usefulness is again derived from their plasmonic properties. Solar panels can only make use of light at certain wavelengths but since the plasmon of nano-particles can be tuned through controlled synthesis the nanoparticles can be made to absorb light at frequencies that are unavailable to the solar panel and release light with frequencies that are available to it. Similar approaches have also been used for other metallic nano-particles.

Another important application of Au NPs is as wiring in nano-circuitry[7], ever since Moore's law was formulated in 1965, great interest has been put into making circuits progressively smaller, leading towards circuits on the nano-scale. Gold nano-wires have been suggested for use in this application as they show lower resistivity and are less susceptible to oxidation than nano-wires of other materials.

As stated above this thesis will attempt the synthesis of three shapes of Au Nps; the gold nanosphere (Au NS), the gold nanorod (Au NR) and the gold nanocube (Au NC) using the seed-mediated growth technique.

In the seed mediated growth technique a seed-solution of small spherical nanoparticles are prepared ahead of time and are then grown into the desired shape by the addition into a solution of the appropriate chemicals.

Beyond the synthesis of these three shapes of AuNPs, this thesis will also attempt three experiments meant to cast some light on the complexities of synthesis of Au NPs.

Firstly, in chapter 2.1.1 the Brust two-phase method will be analyzed and in chapter 3.2.1 an experiment is presented designed to test the current view of the processes that drive synthesis in this method the results of this experiment are shown in chapter 4.1 and these results are discussed in chapter 5.1

Secondly, in chapter 2.1.2 the growth mechanism of CTAB capped AuNRs is analyzed with special focus on the influence of silver nitrate on nanorod elongation. In chapter 3.2.2 an experiment is presented meant to investigate how silver nitrate influences nanorod growth. The results of this experiment are shown in chapter 4.2 and these results are discussed in chapter 5.2.
Thirdly, in chapter 2.1.3, a brief theoretical background to the synthesis of AuNCs is provided. In chapter 3.2.3 a protocol for the synthesis of AuNCs is presented and compared to a similar protocol for making AuNRs. In chapter 4.3 the results from the characterization of these two AuNPs are shown and this is then used, in chapter 5.3 to make a comparison between the two and to make some general remarks about the synthesis of AuNPs.

2 Theoretical background

This chapter aims to explain the physical and mechanistic processes involved in nanoparticle growth for each of the three shapes of nanoparticle that will be synthesized, as well as to outline the principles at work in the characterization methods.

2.1 Synthesis

2.1.1 Synthesis of Nanospheres

The sphere is the easiest shape to synthesize as it is favored by entropy, in principle all that is needed to produce spherical Au NPs is the reduction of some chemical compound containing gold. The commonly used compound is chloroauric acid (HAuCl$_4$). However the Au NPs must not grow too large or aggregate, since in that case they would lose the nanoscale properties which are the purpose of the synthesis. Therefore we must have some capping-agent, that is a chemical that binds to the surface of the Au NP and hinders further growth and aggregation.

Some commonly used methods for the synthesis of spherical Au NPs are the Turkevitch method and the Brust two-phase method. The Turkevitch method uses sodium citrate as both reducing agent and capping agent and produces Au NPs of around 20 nm diameter. The Brust two-phase method on the other hand uses thiol-ligands as capping agent and primary reducing agent and sodium borohydride (NaBH$_4$) as secondary reducing agent in a two step reduction of the gold ions. It is called a two-phase method since it uses both a water phase and an oil phase, the reason being that the thiols used are not soluble in water, whereas the HAuCl$_4$ is not soluble in the oil. In order to bring the HAuCl$_4$ to the oil phase a phase transfer agent must be used, this role also is filled by TOAB, this will be described in more detail in the following section. The Brust two-phase method is popular because it allows control of particle size by variation of the ratio of HAuCl$_4$ and NaBH$_4$. This is also the method used in this thesis.

A more in depth analysis of the reactions that drive synthesis in the Brust two-phase method is as follows:[8][9]

The TOAB binds to the gold precursor at the interface between the two phases (TOAB has one hydrophilic and one hydrophobic end and will therefore lie at the surface between the water and the oil, while HAuCl$_4$ is hydrophilic and will lie in the water) forming a larger complex. These complexes aggregate and form an inverted micelle, with the hydrophobic tails of the TOAB pointed out. These inverted micelles, with the gold ions trapped in them, are then able to travel freely in the oil phase. At the same time the gold is reduced from Au(III) to Au(I), the reduction process is described by the formula:
TOAB+HAuCl\textsubscript{4}→[TOA]AuX\textsubscript{2}+3HX

Where X is an anionic ion, either bromide or chloride. And the additional hydrogens are picked up from the dodecanethiol through the reaction:

2RSH→RSSR+2H

The thiols abandon their hydrogens in order to build a disulfide bond.

Looking at the reduction reaction we see that since H\textsuperscript{+} and TOA\textsuperscript{+} are plus one cations while Cl\textsuperscript{−} and B\textsuperscript{−} are negative one anions the gold is reduced from plus three cations to plus one cations.

In order to further reduce the gold ions from Au(I) to Au(0) or metallic gold the strong reducing agent NaBH\textsubscript{4} is added to the solution NaBH\textsubscript{4} is hydrophilic and will dissolve in the aqueous solution. However intense stirring can cause it to come into contact with the gold ions despite of this fact.

The hydrophobic dodecanethiol diffuses through the TOAB micelle and binds to the metallic gold with the very strong covalent thiol-bond, stably capping the nanospheres.

The process is illustrated in figure 1.

![Diagram of gold nanosphere synthesis](image)

Fig. 1The schematic shows the steps of gold nanosphere synthesis in the Brust two-phase method. [11]

### 2.1.2 Synthesis of Nanorods

The nanorod is not as easily synthesized as the nanosphere since it requires anisotropic growth, a reaction which does not happen spontaneously. Several different methods have been used to overcome this issue. Some of the most popular ones are synthesis in templates, seed-mediated growth in solution and non-seeded growth in solution.

Synthesis in templates can be subdivided into two different categories; synthesis in hard templates and synthesis in soft templates. Hard templates are ready made nanoporous materials commonly aluminium oxide membranes. The nanoparticle is produced either by chemically reducing the gold precursor inside the template pores or by electrochemical deposition of the gold precursor on the templates[10]. Soft templates are, for instance, rodlike micelles and certain surfactants. The shape of the rodlike micelle, and the specific binding behaviour of the surfactants promotes the anisotropic growth of the nanoparticles[11].

Seed-mediated growth and non-seeded growth are both wet chemistry methods. The difference is that in the seed mediated growth method gold seed particles are
produced first and are then used to catalyze the synthesis of gold nanorods whereas
the non-seeded methods synthesize the rods in a single step. In short, both these
methods mix the gold precursor with some capping agent that promotes anisotropic
growth. For gold, cetyl trimethyl ammonium bromide (CTAB) is commonly used.
CTAB promotes anisotropic growth because it is less likely to stick to the edges
than the sides of the growing nanorod, allowing more gold ions to assemble at the
ends of the rod. The reason for this preference is that the spacing of the gold atoms
is closer to the size of the CTA\(^+\) headgroup that binds to the gold at the (1,0,0)
plane than at the close-packed (1,1,1) plane of the Au NP[12]. In the seed mediated
growth method, relatively weak reducing agents such as ascorbic acid are sufficient
for the seed-mediated growth mechanism since the gold seeds act as a catalyst. In
the non-seeded method, the strong reducing agent NaBH\(_4\) is commonly used to
induce nucleation and a weaker reducing agent is used to promote growth as in the
seed-mediated growth method.

In addition, it has been shown that adding silver nitrate to the growth solution
promotes the synthesis of higher aspect nanorods. It was long believed that this
effect was due in some way to the effect of the silver ions. However, it is now
understood that it is due to electrostatic screening of the CTA\(^+\) ends of the CTAB
molecules by the NO\(_3\)\(^-\) ions, making the binding of additional CTAB molecules to
the gold particle more thermodynamically favorable[13]. The CTAB capping
process is illustrated in fig. 2.

Fig. 2: Cartoon illustrating “zipping”: the formation of the bilayer of CnTAB (squiggles) on the nanorod
(black rectangle) surface may assist nanorod formation as more gold ions (black dots) are introduced.[14]

The seed mediated method was used in the experiments as it has many
advantages including the facility that comes with the wet chemistry approach; no
prefabricated templates are necessary. In addition, it has been shown to give a good
yield of nearly mono-disperse nanoparticles[12].

In fact, two different seed-mediated methods were used in experiments, a one-
step method and a multi-step method. The multistep method is devised as a means
to minimize the amount of impurities in the form of spherical nanoparticles in the
nanorod solution. This is done by the result of one growth solution as seed for
another. All nanoparticles that already show anisotropic growth will continue to do
so while those that do not will have a second chance to grow anisotropically.
2.1.3 Synthesis of Nano-cubes/ Nano-cages

The most common way of synthesizing AuNCs is by reducing gold ions onto a silver nano-cube which is oxidized in the process, leaving a hollow gold cube. At high concentrations of HAuCl$_4$ the nanocubes turn instead to porous nano-cages.

Silver nano-cubes in turn, are synthesized by reducing silver nitrate using NaBH$_4$ as reducing agent and PVP (polyvinylpyrrolidone) as capping agent.

There are also many methods that make the AuNCs directly through seed-mediated growth. One of these emphasizes the fact that one of the main impurities in seed-mediated synthesis of AuNRs are AuNCs, and seeks to maximize the extent to which this biproduct appears. This is the method that was used here.

2.2 Characterization

UV-vis-NIR Spectrometry

Perhaps the most practical method of characterizing metallic nanoparticles is UV-Vis-NIR spectrometry. UV-Vis-NIR spectrometry measures the degree at which light is absorbed by a medium at different wavelengths in the ultraviolet, visible and near infrared spectra. This is done by irradiating a sample with light of known wavelength and intensity and measuring the intensity of the transmitted light. The wavelength of the light is varied by the turning of internal prisms.

The machine used was a lambda 750 Perkin Elmer spectrometer. In order to achieve strong intensity light over the entire UV-Vis-NIR spectrum it uses two different lamps, the first one a tungsten-halogen lamp which irradiates strongly at wavelengths in the NIR - visible spectrum and the second a twin deuterium lamp which irradiates strongly at wavelengths in the ultraviolet spectrum. The machine has slots to simultaneously measure two samples, where one is used to test the absorption spectrum of the “background” and one for the actual sample. The background is generally the medium in which the sample is suspended, toluene and water were used in this work.

In the case of metallic nanoparticles we expect to see absorption peaks at the wavelengths corresponding to plasmon excitation. For instance spherical gold nanoparticles generally have a single absorption peak in the 500-600 nm range, while rod-shaped gold nanoparticles have two peaks, one for the transverse and one for the longitudinal plasmon.

Dynamic Light Scattering

Dynamic light scattering (DLS) is a technique which measures the light intensity reflected of particles in solution. The reflected light will change over time as the particles undergo Brownian motion and move away from their original positions. How fast this happens depends on the hydrodynamic radius of the particles (the particles are assumed to be spherical). Therefore measurement of the rate of change of the reflected light can tell of the size of the suspended particles. The results of DLS are presented as a graph of intensity of reflected light over the
3 Method

3.1 Materials

All chemicals were of analytical grade and used without further purification. Chloroauric acid trihydrate (HauCl$_4$ * 3H$_2$O) Cetyl trimethyl ammonium bromide (C$_{16}$TAB, 99%), sodium borohydride (NaBH$_4$, approx. 98%), Chloroform anhydrous (CHCl$_3$) and L-ascorbic acid (C$_6$H$_8$O$_6$) were obtained from Sigma Aldrich. Trisodium citrate dihydrate (Na$_3$C$_6$H$_5$O$_7$*2H$_2$O) was obtained from KEBO. Silver nitrate (AgNO$_3$) was obtained from Alfa Aesar Tetraoctyl ammonium bromide (TOAB) was obtained from Aldrich. Dodecanethiol (CH$_3$[CH$_2$]$_{11}$SH) was obtained from Fluka. Toluene (C$_7$H$_8$) and sodium nitrate (NaNO$_3$) were obtained from Merck. For all reactions Milli-Q water was used and all glassware was rinsed with deionized water prior to the experiments.

3.2 Synthesis of gold nanoparticles

3.2.1 Gold Nanospheres

Two batches of AuNS were made (samples A and B) using different amounts of dodecanethiol in order to find evidence for or against the theory presented in chapter 2.1.1. If it is true that the dodecanethiol reduces a TOAB – gold complex instead of binding to the gold directly, then it is expected that nanoparticles occur only when more than two equivalents of dodecanethiol is present. However if this is not the case, and the dodecanethiol instead reduces and binds to the gold prior to the addition of the NaBH$_4$ then we might see Au NSs for lower concentrations of dodecanethiol.

The AuNSs were synthesized using the following protocol.

1. In the first step two solutions are prepared, one of 15 mL 25mM HAuCl$_4$ (water phase) and one of 1.1g TOAB (tetra octyl ammonium bromide) suspended in 40mL of toluene.
2. These solutions are then mixed and stirred vigorously for 30 min.
3. A 12.7mL aqueous solution of 192mg NaBH$_4$ is prepared.
4. 170/370 μL (sample A/sample B) μL of dodecanethiol is added to the two-phase mix. The solution is stirred for 30 min.
5. The NaBH$_4$ solution is added to the two phase solution which is then stirred continuously for three hours.
6. After three hours the toluene containing the gold nanospheres is separated from the water.

3.2.2 2-step Gold Nanorods

Three batches of 2-step AuNRs were prepared, one (sample E) with added silver nitrate (AgNO$_3$), one (sample F) with added sodium nitrate (NaNO$_3$) and one
(sample D) without either. If it is true that it is the nitrate ions that facilitate anisotropic growth rather than the silver ions, then we expect to see higher aspect ratio NRs in sample E and F as compared to sample D. If it is in fact the silver ions that facilitate anisotropic growth then we expect this effect only for sample E.

The 2-step AuNRs were synthesized using the following protocol.

1. First citrate-capped seeds were synthesized by mixing a 20 ml solution of 0.25mM HauCl$_4$ and 0.25 mM trisodium citrate.
2. To this solution 0.6mL of ice-cold freshly made NaBH$_4$ was added all at once while stirring. The solution turned brownish red.
3. This capping agent for the seeds was then exchanged to CTAB by mixing a 7.5mL solution of 0.1M CTAB and 0.25mM HAuCl$_4$.
4. Into this solution 50 $\mu$L of ascorbic acid was first added and then 2.5mL of the citrate-capped seed. It is important that this step is made soon after the citrate-capped seed has been produced since citrate is only a weak capping agent and there is a risk of aggregation.
5. Two solutions are now prepared, one 9 ml solution (solution A) and one 45 ml solution (solution B) of 0.1M CTAB and 0.25mM HAuCl$_4$. To solution A we add 50 $\mu$L of ascorbic acid and to solution B we add 250 $\mu$L of ascorbic acid. Additionally 0.45ml of 0.1M AgNO$_3$/ NaNO$_3$ was added in the synthesis of sample E and F respectively.
6. 1mL of the CTAB-capped seed is now added to solution A while stirring and after 15 seconds 5mL of solution A is added to solution B while stirring. Solution B was then kept at 25 degrees for about 24 hours.

3.2.3 Gold Nanocubes and 1-step Gold Nanorods

One batch of AuNCs was made (sample G). The purpose of this batch is to show how very similar protocols can lead to different shape nanoparticles. The results will be compared to the 1-step nanorods. For this purpose a table of the molar concentration of each chemical in this sample and the NC sample is added below.

The AuNCs were synthesized using the following protocol.

1. First 10ml seed solution was prepared by diluting 2.5mL of 1mM HAUCl$_4$ to 10ml and adding 0.273g of CTAB powder.
2. To this solution 0.06ml of 0.1M NaBH$_4$ was added and the solution was stirred vigorously for one minute.
3. A growth solution was prepared by adding 0.2ml of 0.2mM HAUCl$_4$ solution to 4.75ml of 0.1M CTAB.
4. To this solution 0.03ml of 0.01M AgNO$_3$ and 0.032ml of 0.1M L-ascorbic acid were added. The solution was stirred gently after the addition of each component.
5. 0.01ml of the seed solution was added to the growth solution and the solution was stirred gently.

The 1-step AuNRs (sample H) were synthesized using the following protocol.

1. The seed solution was prepared by mixing 1ml of 0.5mM HAUCl$_4$ with 1ml of
0.2M CTAB.

2. To this solution 0.12ml 0.01M NaBH$_4$ was added and the solution was then stirred vigorously for 1 minute.

3. The growth solution was prepared by diluting 5ml of 0.5mM HAuCl$_4$ with water to 10.2ml.

4. To this solution 0.364g of CTAB was added. The solution was then placed in a water bath at 25ºC for 5 minutes.

5. At that point 0.055ml of 0.1M ascorbic acid was added to the solution and the solution was mixed.

6. As soon as the growth solution was prepared, 0.02 ml of the seed solution was added into the growth solution and the final solution was left in the water bath for approximately one hour before allowed to reach room temperature.

Table 1 summarizes the concentrations of the different chemicals used in the synthesis above.

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4 Results

4.1 Gold Nanospheres

The UV-Vis-NIR results for the samples made using the Brust two-phase method are shown in Fig. 3.

![Absorption spectra of Au nanospheres](image)

*Fig. 3. The UV-vis-NIR spectra for sample A and B. The spectra show the amount of absorbed light from incident light at the wavelengths indicated at the x-axis of the plots. “a. u” stands for arbitrary unit.*

4.2 2-step Gold Nanorods

The UV-Vis-NIR results for the 2-step Au NRs (samples D, E, and F) are shown in Fig. 4. The DLS results for samples E, F, and D aged one week are shown in Fig. 5.

![Absorption spectra of Au nanorods](image)

*Fig. 4. These are the UV-vis-NIR spectra for samples D, E, and F as well as the spectrum for Sample D, aged 30 days. The spectra show the amount of absorbed light from incident light at the wavelengths indicated at the x-axis of the plots. “a. u” stands for arbitrary unit.*
Fig. 5 These are the DLS results for samples E and F as well as sample D aged 7 days. The diagrams show the relative amount of reflected light for particles interpreted as spheres of the diameter indicated by the x-axis of the plot.

4.3 Gold Nanocubes and 1-step Gold Nanorods

One Batch of gold nanocubes was made, its UV-Vis-NIR spectrum is shown in Fig. 6 alongside the UV-vis-NIR spectrum of the 1-step gold nanorods.
5 Discussion and Conclusion

5.1 Gold Nanospheres

The theory presented in chapter 2.1.1, that the TOAB acts as phase transfer agent and is active in the reduction process in the Brust two-phase method, predicted that no nanoparticles would be made in synthesis using less than two gold equivalents of dodecanethiol. The results in chapter 4.1 were completely opposite to this prediction. A peak consistent with the presence of Au NSs is seen for sample A but not for sample B, that is at low concentrations of dodecanethiol AuNSs were synthesized but not at high concentrations. The possible reasons for Sample B failing to produce Au NSs are many, the Brust two-phase method is not simple and it is therefore not surprising that some samples should fail. The presence of Au NSs in sample A does not necessarily refute the theory of chapter 2.1.1, it may be that not all dodecanethiol had reacted after 30 minutes when the NaBH$_4$ was added. In such case the NaBH$_4$ would have reduced the Au(III) ions leaving the remaining dodecanethiol free to act as capping agent – producing Au NSs.

5.2 2-step Gold Nanorods

5.2.1 Dynamic Light Scattering

The DLS results show the particle diameters of particles assumed to be spherical in shape. Using them for nanorods the expected result is to find a double peak, one for the long side of the particles and one for the short side. Two of the samples; the aged 2-step AuNRs and the 2-step Au NRs to which NaNO$_3$ was added show this pattern, indicating that they are indeed gold nanorods. The third case, with added AgNO$_3$ does not show this pattern, it instead has 4 distinct peaks. One at a radius of about 10nm, another at about 90nm, a third at 350nm and a forth very wide peak centered at about 6000nm. The first two peaks are similar to those found in the other two samples and may be assumed to correspond to nanorods. The forth peak is on the microscale and is clearly a result of aggregation. The third peak may be due to longer nanorods, or smaller aggregations.

5.2.2 UV-Vis-NIR

The data in fig.5 provides several interesting indications. Firstly the nanorods all show the characteristic double-peak behavior of nanorods to different degrees indicating that they are indeed nanorods.

Upon comparing the three batches made using the two-step method we see that both the addition of silver nitrate and sodium nitrate leads to a redshift in the longitudinal plasmon corresponding to nanorods of higher aspect ratios. The fact that this is achieved by addition of both chemicals provides some evidence to the theory that it is in fact the nitrate ions that are active in nanorod elongation as opposed to the silver ions in silver nitrate. In fact it seems that the same amount of sodium nitrate makes for a dramatically longer nanorod as compared to silver nitrate. This may be accounted for by differences in availability of the sodium ions between the two salts, or
by silver ions are reducing onto the surface of the gold nanorod, making it thicker and reducing its aspect ratio.

Comparing the plots for sample D immediately after synthesis and after a 30 day aging period it can be remarked that both peaks have widened, indicating that the monodispersity of the Au NRs has decreased as the sample aged.

5.3 Gold Nanocubes and 1-step Gold Nanorods

The data in figure 6 shows the different plasmonic behaviors of nanocubes and nanorods. In plot for sample H we see the characteristic second peak behavior of the AuNR, but this does not appear for sample G. Upon examination of the differences in the protocols of synthesis for these two samples three major differences are visible. Firstly sample H uses less of the seed solution than sample G, secondly sample G has less HAuCl₄ in its growth solution than sample H and thirdly sample G uses silver nitrate. Since these two protocols are not different by only one parameter no definite conclusion can be made as to which parameter is crucial in reaching these different results. However since the two samples use almost identical seed solution and are treated similarly it shows that such aspects as stirring rate, the relative concentration of gold to silver ions in the growth solution and temperature may be important.

5.4 Conclusion

In this study three different shapes of gold nanoparticles have been synthesized using wet chemistry. Three simple experiments were made aiming to understand some important aspect of nanoparticle growth. An experiment was made to examine the view that it is TOAB, not dodecanethiol, that reduces the Au(III) ions to Au(I) in the Brust two-phase method, the results were not in line with this view. Evidence was also found that suggests that the nitrate ions and not the silver ions are responsible for nanorod elongation in CTAB capped AuNRs. The silver ions may instead be active in thickening the gold nanorods, as suggested by the high ratio of silver to gold in the gold NSs of Experiment 3. It should also be remarked that although sodium nitrate gives longer nanorods, it is far less commonly used than silver nitrate because silver nitrate provides greater control. The results of experiment 3 also enabled us to hypothesize that stirring rate and temperature may be important factors in the synthesis of gold nanoparticles.

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