Metal nanoparticles

January 25, 2007

1 Objectives

- To synthesize gold nanoparticles using the Turkevich method
- To synthesize gold nanoparticles using a biphasic reduction procedure
- To determine the size of the particles through dynamic light scattering
- To employ size selective precipitation to isolate nanoparticles
- To perform rudimentary ligand exchange chemistries to maker water soluble Au nanoparticles

2 Introduction

Nano has been and continues to be one of the most hyped areas in science and technology today.[1,2] It is a collective realization that interesting chemistry and physics occurs in the perviously unexplored hinterland between the truly molecular (the traditional realm of chemistry and even physics) and bulk matter (the traditional realm of engineers). To illustrate, when gold, silver, as well as other metals and even semiconductors are made small enough, they no longer behave in ways that we are accustomed to seeing. For example, gold no longer has the same bright yellow hue as the Dome outside. Instead it turns purple or even black in color!

The same applies to semiconductors such as CdSe or CdTe. Bulk CdSe and CdTe look black. By contrast, when they are made nano-sized their colors turn yellow, orange and red. (Their corresponding emission also exhibits a range of colors that span the visible part of the spectrum. See Figure 1) In fact it is these absorption colors that give rise to the colors in medieval stained glass windows or the yellow hues in early Renaissance paintings. Specifically, CdS and CdSe are well known pigments in “cadmium yellow” paint. As stated in a comprehensive treatise on the development of cadmium pigments[3], “pale [yellow] shades could be prepared by partial precipitation from cold dilution solutions of cadmium slats or by rapid precipitation from acid solutions… very light hues could be attained using cadmium nitrate and sodium sulfide or ammonium thiosulfate.” In these preparations, the color changes experienced by such cadmium chalcogenide compounds are almost certainly a manifestation of so called "quantum confinement" effects. This means that early 19th century pigment chemists were unknowningly synthesizing nanoparticles, taking advantage of their unique size-dependent properties.

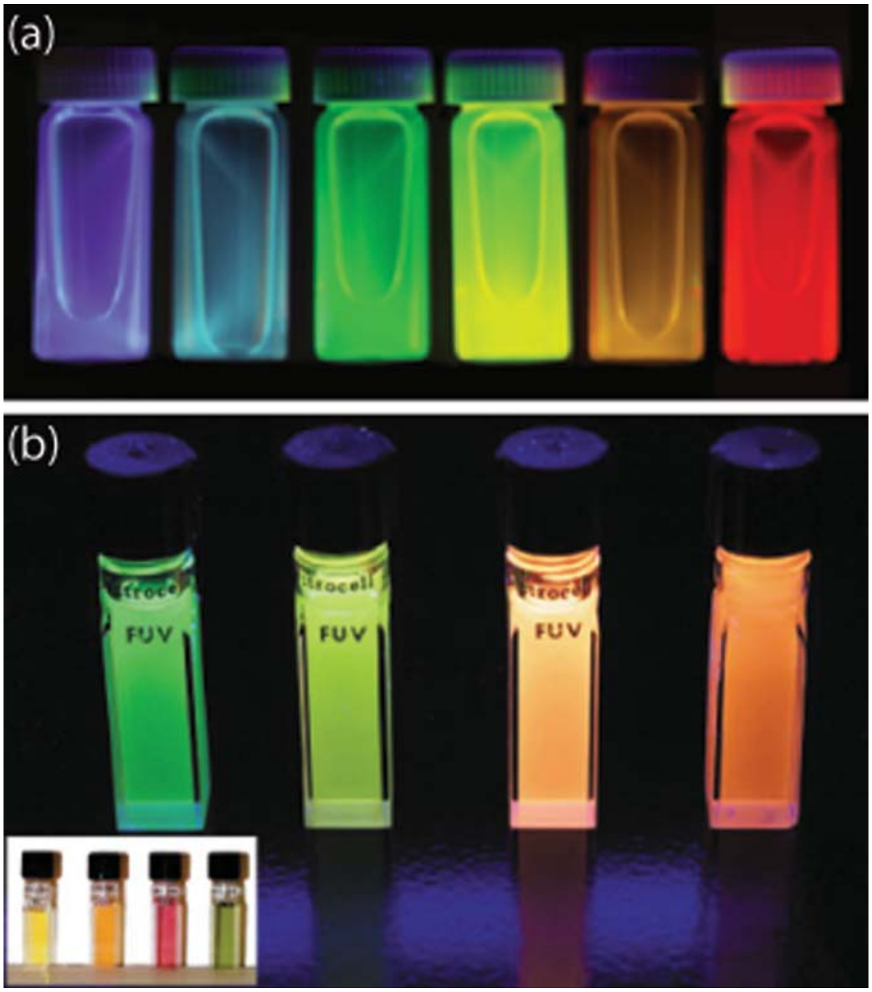

Figure 1: Size dependent emission from a small size series of (a) CdSe and (b) HgS NCs

In fact, we have been living with and dabbling with nanomaterials for quite a long time, nearly 2000 years. Examples include the gold nanoparticles in the Roman Lycurgus cup (4th century AD), the iron oxide nanoparticles in Maya blue paint[4] (approximately 700 AD) and Michael Faraday's colloidal gold solutions, first reported in 1857.[5] Notably these particles are still stable and are on display in the Royal Institution in Great Britain. You can visit this display if you go abroad in your junior year. The difference today, however, is that we are beginning to understand how to control the optical and electrical properties of matter through the deliberate chemical syntheses of high quality nanomaterials. In turn, we are beginning to see new and interesting physics at the nanoscale-physics which can potentially be exploited to make new types of electronics and other devices.

Of course all of this takes time and money. But more importantly it takes people with the right chemical knowledge and intuition to spur further advances in the field. This is where you come in. By doing these experiments it is hoped that you will begin to get a "feel" for the behavior as well as chemistry of nanomaterials. Perhaps this will encourage you to one day contribute to advances in this rapidly growing area.

2.1 What's in a name

Nanomaterials go by a variety of names (nanoparticles, nanocrystals, nanocrystallites, 0D materials and colloidal quantum dots). Often in the literature these terms are used interchangeably and in some cases can result in confusion. Here we briefly describe one (our) suggested naming convention for small (spherical) nanometer-sized materials made of metals and semiconductors. In particular, we will use the term "nanoparticle" (NP) as a generic description for either spherical metal or semiconductor particles with nanometer-sized diameters. However, more often than not, we will use it to refer to metal particles. The name "nanocrystal" (NC) or "nanocrystallite" is often used in conjunction with semicondutor particles and as such will be reserved exclusively for these materials. The term quantum dot (QD) comes from the physics literature where additional names for nanocrystals exist as described below.

In physics parlance, nanocrystals are often referred to as "zero dimensional" (0D) materials. This is because the simplest model of a nanocrystal is the "particle in a box" problem in quantum mechanics. If you are unfamilar with this model problem, don't worry. You will see it soon enough. The idea is that once you make a material physically small, the boundaries of the material begin to "squeeze" electrons (and holes) within the object. This, in turn, changes the electronic energy levels of the structure. So whereas electrons in bulk materials are "free" to roam about the crystal, in nanoscale materials the physical size of the object restricts the motion of these carriers. Thus, depending on how many of the three Cartesian coordinates (x, y, z) the electrons are squeezed in or conversely how many "degrees of freedom" they have, physicists will call the system a two dimensional material (this is a thin film with 2 degrees of freedom for carriers within the plane of the material), a one-dimensional material (also called a nanowire with 1 degree of freedom representing the length of the wire) and a 0-dimensional material (a nanocrystal, it has no degrees of freedom since the electron is completely trapped along x,y and z directions). Finally just like chemists, physicists have other names for 0D materials. The most common name is the "quantum dot". So when we chemists talk about quantum dots we sometimes call them “colloidal quantum dots” to distinguish them from physicist’s quantum dots, which are made using more expensive machinery. Alternatively, physicists sometimes call nanocrystals “artificial atoms” because discrete atomic-like transitions are expected in their optical and electrical properties.

2.2 Gold nanoparticles

In this laboratory we will be making gold nanoparticles with sizes on the order of $\sim$ 10 nm. We will use two approaches to make this material to illustrate some important chemical aspects of nanomaterials. Namely that there exists a variety of ways for making a given material. The first route we will use is an aqueous preparation developed by Turkevich[6] (hence the name of the procedure). Figure 2 illustrates several low resolution TEM images of Au NPs made this way. Accompanying high resolution TEM images (HRTEM) of the same particles are shown in Figure 3. The second approach is an organic phase synthesis in toluene developed by Brust.[7]

Next, after making these materials we will illustrate that the NP surface is very important for a number of reasons. In particular, without something to prevent the particles from touching during growth, large uncontrolled NP aggregates will form. This would then prevent the development of a uniform size distribution for the resulting ensemble. In particular, two particle stabilization schemes, steric and electrostatic stabilization, are illustrated. Next, these ligands are important because they provide solubility to the NPs in either aqueous or organic media depending on the hydrophobicity or hydrophilicity of the surface molecules.

Finally, we aim to illustrate that a good fraction of atoms reside on the NP surface. This can be seen by calculating the fraction of surface atoms in the particle. You may be surprised to find that in some cases nearly 50% of the atoms in a NP are surface atoms. Because these atoms prefer to make bonds to other atoms, the abrupt termination of the NP makes for an odd situation in terms of the NP optical and electrical properties. To amend this situation, NP surface atoms often “reconstruct” in order to maximize their atomic bonding. However, the organic surfactants on the NP surface can also satisfy some of this unfulfilled surface bonding. These ligands therefore contribute to the “electronic” passivation of a nanomaterial.

2.3 Nanoparticle anatomy

Figure 4 shows a cartoon depiction of a typical colloidal NP. In particular, it consists of two main parts. The first is the core and the second is the outer organic stabilizing layer. The core can be made out of a variety of materials and in this laboratory it will be made of Au. It is also the core which dictates the optical and electrical properties of the NP. As described earlier, the core acts as a “box” which confines electrons to the physical dimensions of the particle. This leads to well known quantum “confinement” effects dictated by quantum

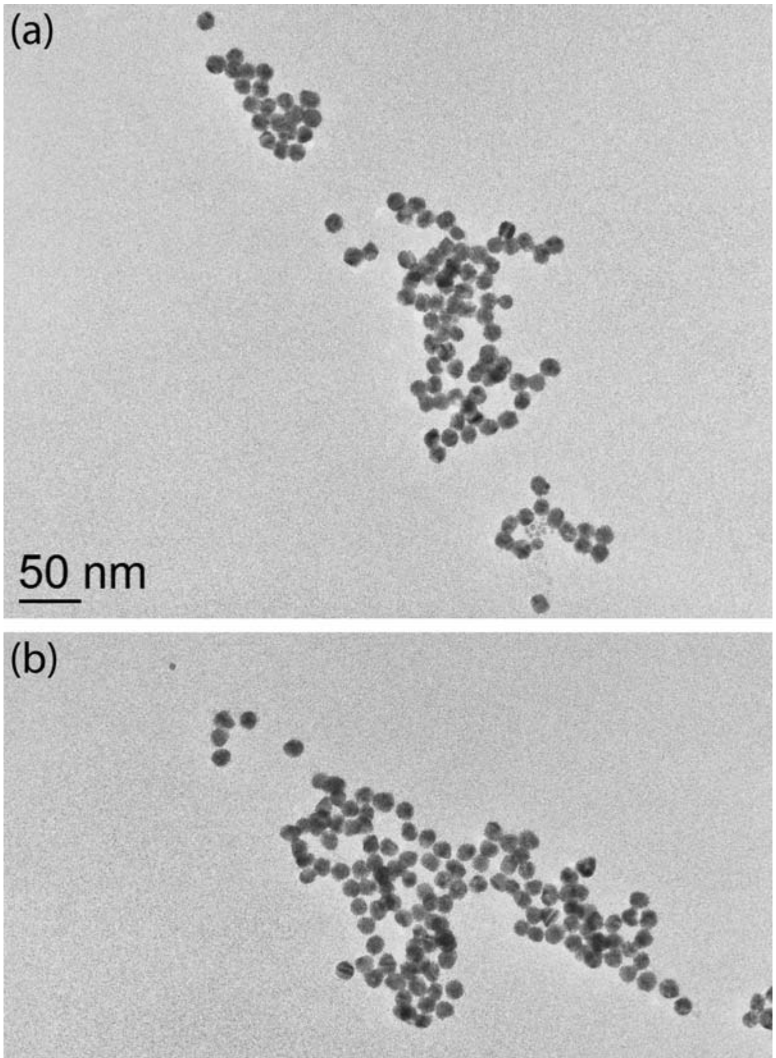

Figure 2: Low resolution TEM micrographs of Au NPs.

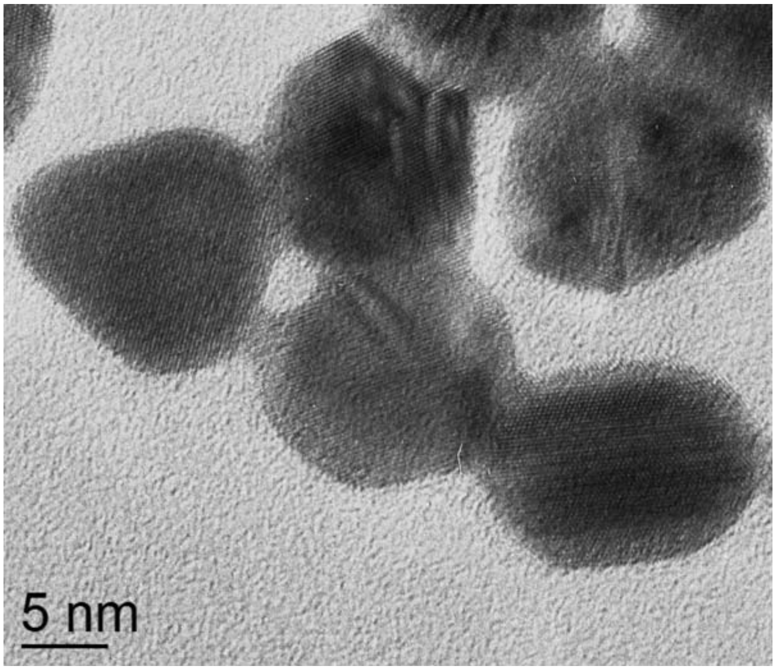

Figure 3: High resolution TEM micrograph of Au NPs.

mechanics. In conjunction with X-ray diffraction measurements, it has been determined that the core is nearly identical to the crystal structure of the parent (bulk) material. As a consequence, it is more or less valid to think of the core as a much smaller fragment of the bulk lattice. Furthermore, most of the time the overall morphology of the NP will be spherical. However, cases exist where cubes, rods and other non-spherical shapes have been made through analogous solution chemistry. You can already see some examples of this in Figure 3.

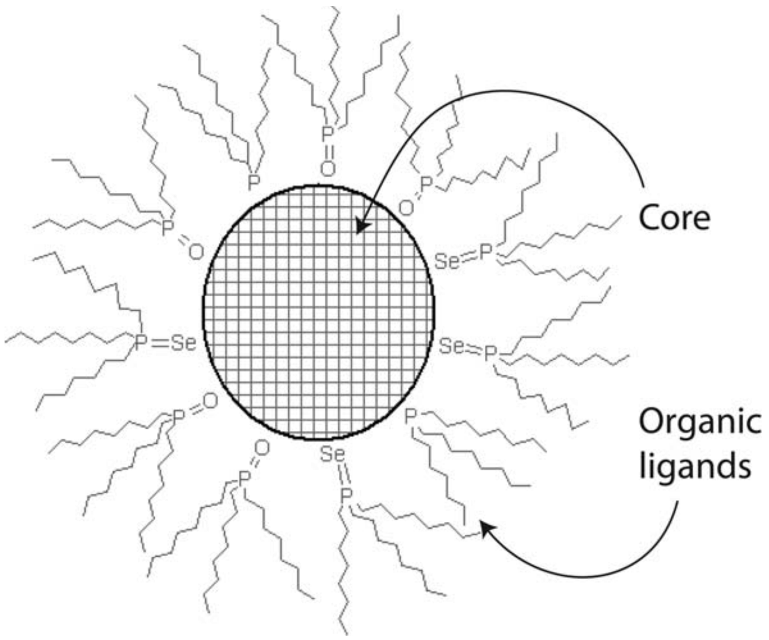

Figure 4: Nanoparticle anatomy

The second major aspect of the NP is its outer organic shell. Specifically, in the solution-phase synthesis of colloidal nanomaterials, some method of stabilizing the resulting structure is needed in order to prevent aggregation (clumping) of the particles. Thus from the homogenization of milk to the "weapon-ization" of anthrax, numerous strategies have been developed by chemists for stabilizing colloidal particles. For some of the NPs discussed here, the stabilizing layer will consist of simple organic surfactants which provide steric stabilization of the particles. NPs in close proximity to each other thus encouter a repulsive potential stemming from surface bound organic molecules. Alternatively, NPs can be stabilized by electrostatic means, relying on the Coulomb repulsion of like charges to prevent particle agglomeration.

The general structure of the organic passivating ligand consists of a head group that "sticks" to the NP surface via dative bonds, actual covalent bonds or electrostatic attraction. The surfactant molecule also possesses a "tail" which points away from the nanoparticle surface, extending into the surrounding liquid medium. This tail is important because its polar/nonpolar nature dictates the NP solubility within surrounding organic or aqueous media. For many chemically synthesized NPs, their primary solubility will be within organic solvents.

Finally, it should be noted that surfactant molecules also provide electronic stabilization of the NP by coordinating to dangling bonds on the surface. These dangling bonds stem from the abrupt termination of the NP core. If not taken into account, they may lead to defect related contributions to the NP optical and electrical properties. As a consequence, for this and other abovementioned reasons, the synthesis and development of colloidal NPs is as much about the growth of the core as it is about the choice of organic surfactants passivating their surfaces.

2.3.1 Somthing to consider

How many atoms do you think make up a 10 nm Au NP? How would you go about calculating this? Turns out that there are a number of ways. Let's outline how you might go about it. We'll leave the other approach for you to figure out. Hint: It uses information about the Au unit cell and its volume.

Outline

- First figure out the volume of a single NP. Convert this number to cm^3 units.
- Use the bulk density of gold ρ_{Au} to determine the weight of a single NP in grams.
- Next using the atomic weight of Au, how many moles of Au makes up a single NP.
- Finally use Avogadro's number to get the number of Au atoms in a single NP.

Next, what do you suppose is the fraction of surface atoms in a 10 nm diameter Au NP? Well, there exits no conventional way to calculate this value. Instead, we will just perform our own calculation in what follows. (This is another example of what is often referred to as a "back of the envelope calculation". Presumably this term originates from the urban legend that physical chemists go to dinner in "fancy" restaurants and in between appetizers start doing calculations on the back of an envelope that we just happened to bring with us.) The basic idea will be to use information about the unit cell of gold to find this value. Note that gold has a cubic FCC crystal structure (Again, if unfamiliar with this concept, it can be looked up.) with a lattice constant of $4.08\AA$ (0.408 nm) and with 4 atoms per unit cell (the calculation of this number is generally taught in undergraduate classes, but if not can be looked up).

Outline Here we will take the approach that there is an outer shell of atoms surrounding the core of the particle. It is these atoms that we want to count. Next, this shell has a finite thickness which we assume is half the lattice constant.

The shell thickness is therefore 0.204 nm. Now the volume of the entire NP will be calculated and from this the volume of the shell will be determined. Since the volume of a unit cell is known the effective number of unit cells making up the shell is determined. Finally, since there are 4 atoms per unit cell the total number of surface atoms can be found.

For a 10 nm diameter Au NP we get the following: The volume of the core after accounting for the finite shell thickness is

$$\begin{aligned} V_{core} &= \frac{4}{3}\pi(5-0.204)^3 nm^3 \\ &= \frac{4}{3}\pi(4.796)^3 nm^3 \\ &= 462 nm^3 \end{aligned}$$

The total volume of a 10 nm diameter NP is

$$\begin{aligned} V_{tot} &= \frac{4}{3}\pi(5)^3 \\ &= 524 nm^3 \end{aligned}$$

The volume of the shell is the difference between the total volume and the volume of the core.

$$\begin{aligned} V_{shell} &= V_{tot} - V_{core} \\ &= 524 - 462 nm^3 \\ &= 62 nm^3 \end{aligned}$$

Now since we found that the lattice constant of the Au unit cell is 0.408 nm the volume of a single unit cell is

$$\begin{aligned} V_{unit} &= (0.408)^3 nm^3 \\ &= 0.068 nm^3 \end{aligned}$$

This enables us to determine the number of unit cells making up the shell from

$$\begin{aligned} Unitcells_{shell} &= \frac{V_{shell}}{V_{unit}} \\ &= \frac{62}{0.068} \\ &= 912 \end{aligned}$$

Since the number of atoms per unit cell is 4 we get the total number of surface atoms

$$\begin{aligned} Atoms_{surface} &= (912)(4) \\ &= 3648 \end{aligned}$$

Now we need the total number of atoms in the entire particle. To get this value we find the total number of unit cells.

$$\begin{aligned} Unitcells_{tot} &= \frac{V_{tot}}{V_{unit}} \\ &= \frac{524}{0.068} \\ &= 7706 \end{aligned}$$

The number of atoms per unit cell is 4 giving the total number of atoms in the particle (oops did I just give away the second way of calculating the number of atoms in a particle? How does this number compare to the first approach?)

$$\begin{aligned} Atoms_{tot} &= (7706)(4) \\ &= 30824 \end{aligned}$$

Thus, from this we can find the fraction of surface atoms

$$\begin{aligned} f &= \frac{Atoms_{surf}}{Atoms_{tot}} \\ &= \frac{3648}{30824} \\ &= 0.12 \end{aligned}$$

So 12% of atoms in the particle are on the surface. What about the case of a 2 nm diameter particle? What do you suppose the surface atom fraction will be here?

2.4 Sizing nanoparticles

Perhaps the most important task at hand when making and characterizing nanoscale materials is to control the size of the particle. To an equal extent we also want to control the shape of the resulting material. Both are important parameters because as described earlier, nanoscale metals and semiconductors exhibit size and shape dependent optical, electrical and even chemical properties.

The next most important task after making nanoscale materials is to determine their size. In this respect, a number of ways exist for sizing nanoscale materials. In the present laboratory we will use one of the techniques described below (dynamic light scattering) to verify the size and size distribution of chemically synthesized Au NPs. We will also provide images from another technique so that you can actually "see" what the particles look like. Furthermore, you will use these images as an independent way to size the particles and will verify that the two techniques provide similar values of the NP diameter. We will briefly describe the other techniques so that you know that they exist and that they are routinely used by practicing chemists/physicists.

Transmission electron microscopy (TEM): This is the most common technique for "looking" at nanoscale materials. It is analogous to conventional light microscopy that you see on TV shows such as CSI (note that CSI plugs Zeiss) or Crossing Jordan. However, TEM uses electrons instead of photons to image samples. In addition, electromagnetic instead of glass lenses are used to focus a beam of electrons on the sample. The transmitted electron beam is then re-imaged on a detector to reveal a picture of the specimen. Because the classical diffraction limit of an electromagnetic wave is roughly half its wavelength, a beam of electrons resolves much finer things than photons (i.e. light). Despite its power, we will not use an actual TEM in this laboratory because of time constraints involved in teaching someone to use this instrument. It is also not conveniently available at the current time. Instead we have provided sample TEM images in Figures 9 to 18 to enable you to see the particles and to size them using the provided scale bar. This is done in practice by creating a histogram of sizes and fitting the histogram with a Gaussian function. (If you are not familiar with the Gaussian function you can look this up.) An example of this sizing procedure derived from the images provided is shown below in Figure 5. Over 150 particles were measured. The resulting mean particle diameter is 14 nm with a standard deviation of 1 nm. The estimated ensemble size distribution is 7% which is actually pretty good.

Scanning probe microscopy (SPM): Another approach that can be used to determine the size of nanoscale materials involves scanning probe microscopies such as atomic force microscopy (AFM). An AFM is akin to a stylus or a needle on an old record player. In this respect, a sharp pointed tip is raster scanned over a sample to "feel" out the bumps and features of a nanoscale object. Changes in the height of the tip are recorded and an image of the material is subsequently reconstructed based on these fluctuations.

The primary disadvantage of an AFM is that the tip has a finite radius of curvature (i.e. it is not infinitely sharp). As a consequence, size measurements of nanoscale objects are made difficult because the recorded width includes the width of the tip (called tip convolution). The technique is also somewhat slow since it is a scanning technique (i.e. you take data one point at a time and reconstruct an image point by point). Scan times on the order of 10 minutes are common. Feedback loops must also be introduced if one is to ensure that any sample "drift" is minimized. Thus TEM is generally preferred to AFM since it has an intrinsically higher throughput. We will likely not use this approach because of the lack of a convenient AFM to use. However, future versions of this laboratory may include this option.

X-Ray powder diffraction X-ray diffraction is often used to determine the crystallographic phase and structure of a given material. The underlying idea of this technique is that atomic planes in a crystal will diffract incoming X-rays. Thus depending on the actual arrangement of atomic planes in a material, characteristic X-ray reflection lines at different angles of the incident beam relative to the specimen will appear. Often these reflections and their exact angular positions are characteristic of a material. These X-ray diffraction patterns can therefore be used to fingerprint a given material. Tables of X-ray reflections lines are tabulated in numerous databases to aid in this effort.

When dealing with nanoscale crystalline materials, the width of the X-ray

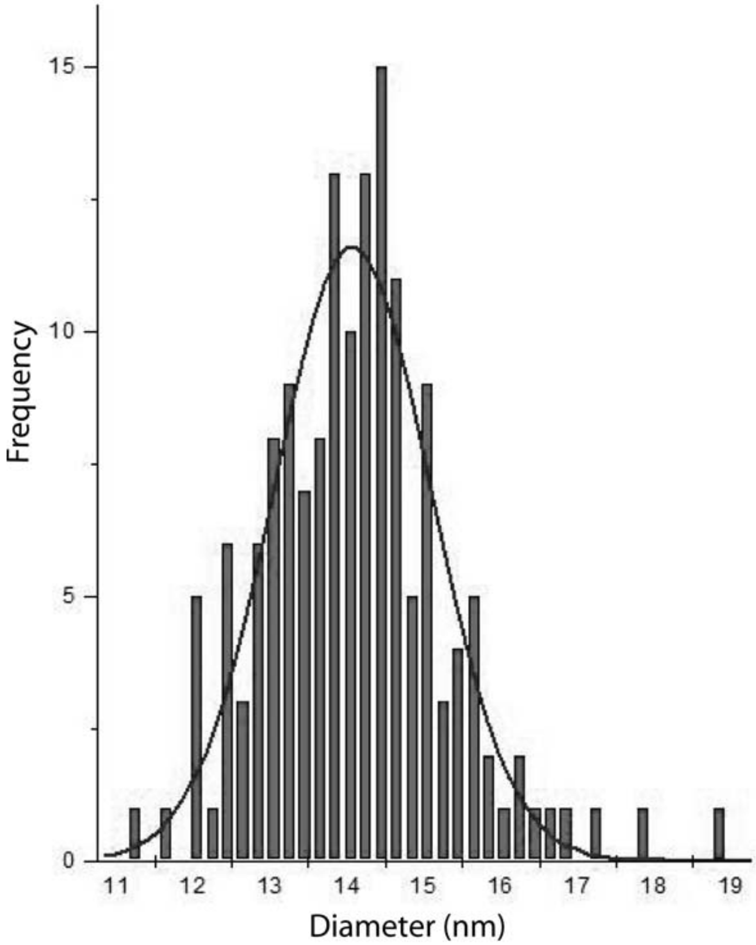

Figure 5: Ensemble size histogram

reflection contains additional information that can be used for sizing purposes. In particlar, the width of the X-ray line is related to the average NP size through the Scherer equation.

$$d = \frac{0.9\lambda}{B cos\theta} \tag{1}$$

Here d is the dimension of the grain (in our case this is the NP diameter), λ is the wavelength of the incoming X-rays, B is the breadth of the peak (or full width at half maximum, FWHM) in radian units, and θ is the half angle of diffraction. By plugging in the appropriate numbers taken directly from X-ray diffraction data the size of a NP ensemble can be estimated quickly. However, we will not use this approach to size particles because we currently lack convenient access to a X-ray diffractometer.

2.5 Light scattering

The phenomenon of light scattering by colloidal particles dates back many centuries. A narrow beam of sunlight reveals the presence of dust particles in the atmosphere because of the scattering of light. The first to try to study this phenomenon systemiatically as a scientific question was again Faraday using his well-known gold particles. Studies by Tyndall that followed led to the Tyndall effect that reveals the Brownian motion of particulate dispersed in a fluid medium. Lord Rayleigh conducted the first rigorous theoretical study of light scattering by small particles in 1871, which was followed by the landmark extension of the theory by Mie in 1908. The phenomenon can be treated classically using the electromagnetic nature of light and requires no quanum mechanical intervention (although a quantum mechanical treatment, of course, leads to the same results). In spite of the long history and deep understanding of this phenomenon, the determination of physical parameters that affect the intensity of the scattered light, such as size and shape, still remains extremely complex problems. Nonetheless, recent developments in laser technologies, sophisticated data acquisition electronics, and the evolution of computational power, combined with algorithms for elaborate numerical analysis of experimental results, have advanced this field tremendously. It is possible at present to obtain not only the size of particles but also their size distribution, shape, diffusion coefficient and surface electrical potential (more precisely, their zeta potentials) utilizing this tool. We will only address spherical particles in this laboratory though. The interested student may find much more information on this area of science and technology in most physical chemistry textbooks or in the exhaustive treatment by Kerker.[8]

Why is light scattered? To understand the basic principles of the phenomenon we will discuss small particles. These will be particles whose diameter is smaller than the wavelength of light by say a factor of 10-50. As we all recognize at this stage, radiation can be represented through a fluctuating electric field perpendicular to the direction of the light propagation (more technically, the direction of its so called Poynting vector). The electric field oscillates at a characteristic frequency. Furthermore, since light is an electromagnetic wave, there also exists a (phase shifted) complementary magnetic field which also oscillates at the same frequency. Like the electric field, it is oriented perpendicular to the Poynting vector. Figure 6 provides a schematic presentation of the light propagation and of the general arrangement (geometry) for observing light scattering.

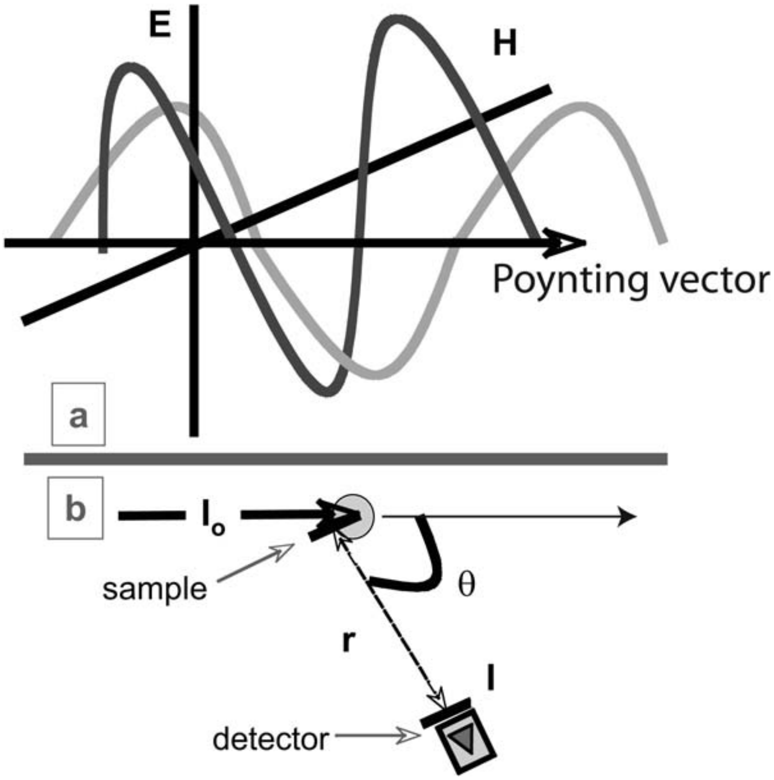

Figure 6: a) Top - Schematic representation of electromagnetic radiation propagating in the direction of the arrow as the oscillating electric field (E) is at right angles to the magnetic field (H). b) Bottom - Basic principle of the experimental setup for measuring light scattering. The detector (triangle) is in the plane of the paper at an angle to the direction of the propagation. I_o and I are the intensities of incident and scattered light respectively.

Next, as light propagates through matter, the electrons of the material will respond to its oscillating electric field. In this section, we will not be concerned with the *absorption* of light (for example, the quantum mechanical raising of the electron to a higher energy state via the absorption of a photon) or with "inelastic" light scattering (i.e. scattering that involves the exchange of energy between the incident light and the scattered light) such as *Raman scattering.*

Depending on the so called “polarizability” (generally denoted by α) of the material, the amplitude of the oscillating electrons can either be large or small. Obviously the bigger α is the larger the oscillation amplitude. Oscillating electric fields (e.g. from the electrons) are equivalent to waves of light and because the frequency of the oscillating electrons is the same as that of the incident light. The scattered light therefore has the same wavelength as the incident light; the scattering is *elastic*. Its intensity, of course, is much weaker. More information on light scattering can be found in Reference [9].

How intense is the scattered light and how is it distinguished from other forms of light-matter interaction (e.g. fluorescence)? The intensity of the scattered wave I at a distance r from the light source (Figure 6b) is proportional to the square of the polarizability, α, of the particle and is inversely proportional to r^2. It can be shown that the ratio of the scattered light intensity (I) to the incident light intensity (I_o) in the plane normal to the direction of the polarization of the light is given by

$$\frac{I}{I_o} = \frac{16\pi^4}{r^2\lambda^4}\left(\frac{-\alpha}{4\pi\epsilon_o}\right)^2 \tag{2}$$

where λ is the wavelength of light and ϵ_o is the permittivity of free space ($\epsilon_o = 8.854 \times 10^{-12} F/m$). Now the polarizability of a particle with volume V and refractive index n_1, immersed in a medium of refractive index n_o, is given by

$$\alpha = 3\epsilon_o\left(\frac{n^2-1}{n^2+2}\right)V \tag{3}$$

where $n = \frac{n_1}{n_o}$ is the *relative refractive index*. For spherical particles of radius R, direct substitution of above expressions for its volume and polarizability gives

$$\frac{I}{I_o} = \frac{16\pi^4}{r^2\lambda^4}R^6\left(\frac{n^2-1}{n^2+2}\right)^2 \tag{4}$$

Next, when the light is horizontally polarized, the right hand side of the above equation is multiplied by $\cos^2\theta$ (θ is the angle between the line connecting the scattering particle and direction of light propagation, see Figure 6). When the light is unpolarized and the observation is in the horizontal plane, the intensity depends on the angle. Summation of the contributions from the vertically and horizontally polarized components gives

$$\frac{I}{I_o} = \frac{1}{r^2}\left[\frac{16\pi^4}{2\lambda^4}R^6\left(\frac{n^2-1}{n^2+2}\right)\left(1+\cos^2\theta\right)\right] \tag{5}$$

The factor in square brackets is called the Raleigh Factor (R_θ). When the observation is at 0° or 180° (forward or back scattering) $cos^2\theta = 1$ and both the vertical and horizontal polarized components contribute equally to the intensity. At 90°, $cos^2\theta = 0$ and only the vertical component contributes. So far we considered only a single particle. When the concentration of particles is c per unit volume, the scattering is simply the sum of the scattering by each particle present in the detection volume (this assumes dilute solutions so that multiple scattering of the same photon is ignored).

Limitations: A major limitation of this technique is that it requires that the particle be smaller than the wavelength of light. Another limitation is that it does not consider the effects of shape and furthermore requires dilute solutions. Most of these limitations are dealt with using more advanced theoretical treatments. Most common are the Debye and Gans variants (often called RDG theory) but all of them are beyond the scope of this course. Sizes and shapes of complex molecules (e.g. polymers or proteins) can be quite accurately obtained using numerical computational simulation of the scattering pattern and comparing it with the experimentally obtained patterns. This often requires multi-angle scattering measurements. The one difficulty that remains unresolved is the problem of multiple scattering. Of course, dilution of the sample may minimize this problem but in many situations it is not an option. In any event, you should always try to minimize this effect.

Dynamic light scattering (our primary sizing technique in this lab): If a laser is used in the measurement of light scattering, its coherent light may generate constructive-destructive interference patterns when the light is incident on an ensemble of particles. This is not the case with a conventional halogen or arc lamp because the light scattered from different particles is random in phase relative to light scattered from another particle. The pattern of interference from light scattering using lasers and static particles is, in principle, not any different from X-ray diffraction patterns produced by crystals. However, in suspension the particles are not static. They continuously move. As a result, over a period of minutes during which the experiment is conducted, the interference pattern will change. Such changes may look as flickers of the intensity to the eye.

Now it is these intensity fluctuations which are exploited in dynamic light scattering to indirectly determine the radius of the particles via a determination of their diffusion coefficient. The "twinkling" is sensed by a photon correlator (and thus the technique is often called photon correlation spectroscopy) which enables one to generate a correlation function between the scattering intensity at a time t and at a later time $t + \tau$. When τ is large, the time dependent intensities, $I(t)$ and $I(t + \tau)$, are independent of one another. However, when it is short, they are closely related because the particles haven't really moved much. The resulting correlation function is then a measure of the probability that the particle will move a given distance in time τ. For monodisperse particles (a single size to be precise) the correlation function is a simple exponential

$$g(\tau) = e^{-\frac{\tau}{\tau_c}} \tag{6}$$

where τ_c is a characteristic constant related to the diffusion coefficient, D, of the particle via

$$\tau_c = \frac{1}{DQ^2} \tag{7}$$

Here Q is called the wavevector and is a function of the instrument used and the angle θ of detection, $Q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$.

Plotting $ln(g(\tau))$ versus τ one gets τ_c or D. Then using the Stokes-Einstein equation, one gets the hydrodynamic radius (R) of the particle. (Don't worry, all of this is done by the computer on your light scattering instrument)

$$R = \frac{kT}{6\pi n} Q^2 \tau_c \tag{8}$$

Photon correlation spectroscopy is therefore widely used for determining sizes of colloidal particles in solution. The ease of operation and the ability to do size determination in-situ without the need to dry the solution (an opertion that may change the particle size and cause precipitation of salts that may be dissolved in solution) are its biggest advantages (e.g. relative to microscopies such as TEM). When the size distribution is narrow, TEM and DLS provide similar results. When the distribution is large, they may differ significantly. Why?

Another common application of DLS is to measure light scattering under an applied electric field, i.e. electrophoresis. Because of the Doppler effect, the scattered light from moving particles has a wavelength slightly shifted from that of the incident wavelength. However, despite the tiny magnitude of these shifts, they can be measured. This technique is therefore gaining popularity because of the quantitative information on zeta potentials (surface potentials) that it can provide.

2.6 Size selective precipitation

Now back to chemistry. An important technique for working with chemically synthesized nanomaterials is called "size selective precipitation." Its name originates from its historical development in helping to reduce the size distribution of NP ensembles. However, size selective precipitation is a much more useful and general technique by which to isolate chemically synthesized nanomaterials. Through this approach, powders of NPs can be made. Alternatively, particles can be isolated from one solvent and subsequently redispersed into another medium.

In explaining size selective precipiation we will assume the case of NPs with organic ligands on their surfaces and which are soluble in common organic solvents such as toluene. Under these conditions, the addition of a miscible polar alcohol such as methanol (MeOH) will reduce favorable solvent-surface ligand interactions. This will then lead to the eventual flocculation (i.e. coagulation) of the NPs. Attesting to this, classic claculations by Hamaker show that, to a first approximation, the Van der Waals attraction between two equal sized spheres increases with radius. Therefore if the addition of a polar solvent is sufficiently slow and changes in solvent polarity are gradual, then only the largest NPs present will flocculate. This leaves the smaller sizes still dispersed in solution. By repeated application of this process the size distribution of an ensemble can be reduced. Figure 7 outlines the procedure.

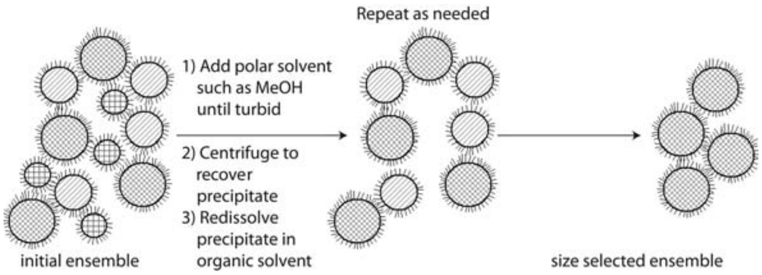

Figure 7: Overview of size selective precipitation

At the same time, if enough non-solvent (i.e. MeOH) is added to the solution, *all* of the particles will fall out of solution. This is then a way to isolate powders of NPs that have been synthesized. The particles can be recovered by centrifiguing the suspension and isolating the resulting precipitate. At this point the particles can be stored as dry powders. Alternatively they can be redispersed in another compatible solvent. Because the NPs are soluble and can be islolated, subsequent ligand exchange chemistries are possible. This enables one to functionalize or alter the surface chemistry of the NPs and is described in more detail in the next section.

2.7 Ligand exchange

Possibly one of the most important distinguishing features of chemically synthesized nanomaterials is the ability to alter their surface passivation. In this respect the solubility of NPs in various organic or aquenous solvents enables surface derivatization chemistries to be developed. For example, organic (hydrophobic) ligands on NP surfaces can be replaced with hydrophilic ligands in order to make the NP soluble in polar or aqueous media. This is because unlike the static picture conveyed by our diagrams, the NP surface ligands are actually in equilibrium with the surrounding solvent. As a consequence, if competing surface binding ligands are introduced into the solution in great excess, they will eventually replace all of the native NP ligands. In this fashion, the surface chemistry of solution-based NPs can be altered at will. In practice, the best way to replace nearly all NP surface ligands is to expose a NP precipitate to the new ligand neat (i.e. not diluted). So if the new ligand happens to be a low melting solid, one mixes the NPs with the solid and heats the resulting mixture to hasten the ligand exchange. Alternatively if the new ligand is a liquid, one disperses the NPs in the new ligand and heats the resulting solution. In either case, after heating, the particles can be precipitated from the mixture using an appropriate non-solvent. The material can then be redispersed in a neutral solvent allowing the resulting surface derivatized material to be characterized.

In the present laboratory, we will replace hydrophobic ligands on the Au NP surface for hydrophilic ligands in order to bring the particles into water.

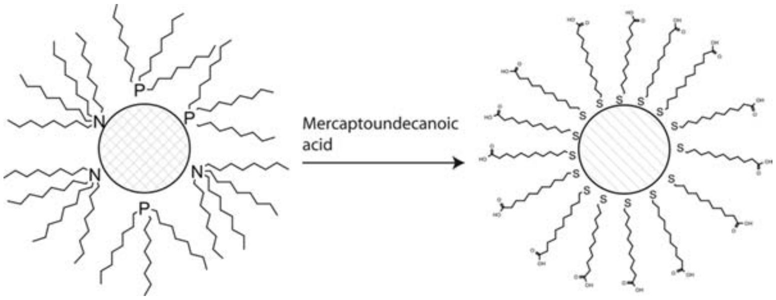

Figure 8: Ligand exchange

A cartoon schematic of the process is shown in Figure 8. It is possible to consider subsequent chemistries to attach biologically relevant molecules to the newly functionalized NP surface. In fact, it is this capability that has attracted significant attention from the biological imaging community. The ability to attach either high contrast metal particles or highly fluorescent semiconductor NPs to cell walls or to proteins has opened up numerous imaging opportunities previously difficult to achieve using conventional organic staining agents or dyes. For example, multicolor tagging experiments can now be carried out in a much more straightforward fashion.

2.7.1 Optional NMR or FTIR characterization

Note that because the surface functionalized particles can be isolated through size selective precipitation and redispersed into a solvent of choice one can pursue additional surface characterization techniques. For example, the particles can be solubilized in deuterated solvents such as toluene or chloroform. The proton (or other nuclei) NMR spectra can then be acquired to characterize the newly functionalized NP surface. Alternatively, if the surface ligands have characteristic IR transitions, FTIR spectroscopy can be conducted on powder or nujol dispersions of NPs.

2.8 Other material

A variety of other nanoscale materials can be made through abovementioned solution chemistry approaches. For example, semiconductor materials from the groups II-VI (CdS, CdSe, CdTe), III-V (InP, InAs) and IV-VI (PbS, PbSe, PbTe) are of particular interest from basic science and applied perspectives. In this respect, such particles may have uses in nanoscale transistors, biological sensors, and next generation photovoltaics. Although most of the syntheses of these nanoscale materials are beyond the scope of this and other undergraduate level laboratories, you will have the opportunity to make CdSe NCs in an upper level inorganic synthesis class taught by Doug Miller.

3 Procedure

3.1 Getting started

Prepare the following stock solutions. When working with gold tetrachloroaureate ensure that any metal spatulas used are covered with teflon tape. Also ensure that you wear gloves and that this chemical does not get on your skin. Clean up after yourself to ensure that no one unexpectedly gets exposed to this chemical. The gold salt will discolor your skin and takes a few weeks before it comes off. Note also that the gold tetrachloroaureate is hygroscopic and will begin to pick up water on exposure to air. Thus the more time spent at the balance the more uncertain the actual weight of the gold salt measured. Finally store any unused gold tetrachloroaureate in the dessicator.

3.1.1 Gold stock solution, Turkevich procedure

Add 0.155 g $HAuCl_4$ to 91 mL of deionized water. The gold salt should dissolve readily in water.

3.1.2 Citrate solution, Turkevich procedure

Add 0.25 g sodium citrate to 50 mL deionized water. As before the salt should dissolve readily.

3.1.3 Gold nanoparticle synthesis, Turkevich procedure

Take 1 mL of the gold tetrachloroaureate stock and add it to 18 mL of deionized water. Use an appropriate sized earlemeyer flask ($\sim$ 50 mL works fine). Now bring this solution to a boil on a hot plate. Also stir the solution with a magnetic stirrer. Wait until the solution is really boiling. Now add 1 mL of the soldium citrate stock while stirring and boiling. Wait for an eventual color change. You will see the solution begin to slowly turn color from clear to a purple-like hue. Wait until the color looks like grape Cool Aid before removing the solution from the hot plate. Let the solution cool to room temperature. Add some more deionized water when cool to bring the total volume up to 20 mL.

3.1.4 Gold nanoparticle synthesis, Biphasic reduction or Brust procedure

Prepare a solution consisting of 0.55 g of tetra-n-octylammonium bromide (TOAB) in 20 mL of toluene. Stir this using a magnetic stirrer. A 125 mL Earlemeyer works for this. Next prepare solution of hydrogen tetrachloroaureate consisting of 0.09 g in 7.5 mL of deionized water. Stir this solution as well. When both solutions are ready, add the colored aqueous gold solution to the TOAB Earlemeyer. Stir this solution vigorously. What you are doing here is using TOAB to extract the Au ions from the aqeuous phase into the toluene organic phase. This is why TOAB is commonly referred to as a phase transfer reagent. Now after approximately 10 minutes of vigorous stirring you should see a nice orange color in the toluene phase. The water phase should be clear. At this point add a solution consisting of 0.095 g sodium borohydride in 6.25 mL deionized water into the Earlemeyer under vigorous stirring. Use an addition funnel and drop this solution over the course of say 30 minutes. (Bottom line, not too fast). Once you have added everything let the resulting solution stir for another 10-20 minutes. When complete, use an addition funnel to isolate the toluene phase. (This is the colored phase with your newly made Au NPs). The aqueous phase can be discarded. Finally add 3 mL of trioctylphosphine (TOP) and stir the resulting solution for several minutes. The phosphine ligand will datively bind to the Au NP surface and will help stabilize the resulting particles.

3.1.5 Using the dynamic light scattering apparatus

We will use the DLS technique to determine the size and size distribution of various particles in (aqueous) suspensions across this Lab course. The same instrument, Beckman-Coulter N4-Plus, will be utilized at all stages.

Instrument specifications: Sizing range: 3 nm - 3 m; Excitation source: He-Ne (Helium-Neon) Laser (632.8 nm); Detection system: 6 - fiber optics located at 14.9°, 20.6°, 30.4°, 40.2°, 50.4°, and 90°. We will use only the 90° angle and assume spherical particles. The software is self-explanatory and an instructions manual will be available from the instructor.

Before you start the measurement, turn instrument on and after a few minutes turn the computer on. The machine needs to warm-up and the temperature in the cell compartment equilibrated with the sample (approximately 15 minutes) before you can perform the measurements. The computer will report that the machine is ready.

Experiment 1: Test a blank of the water you used in the synthesis. Then, before any measurement of your own samples, receive an unknown calibrated standard-size suspension sample from the instructor. The instructor will verify beforehand that the concentration of particles in the unknown (to you) standard is low enough to minimize multiple scattering, yet allow good signal-to noise-ratio. Measure the size (might contain several size populations) and size distribution of the standard and report to the instructor. When confirmed by the instructor you may proceed to your own samples.

Experiment 2: Use your own samples from the synthesis above or later experiments as the course progresses. Determine by simple dilutions the appropriate concentration for you sample. Dilute the sample until two consecutive dilutions give the same sizes. Once you have the right concentration perform three repetitive measurements and report the average size and the witdh at half maximum of your size distribution. Turkevich reports $r = 15$ nm for his citrate stabilized particles; how close are you to his values?

3.1.6 Size selective precipitation

To illustrate size selective precipitation, start with the TOP passivated Au NPs dispersed in toluene (see above). To this solution add increasing amounts of methanol while stirring the mixture. As you add the MeOH you will see the solution go cloudy. This is due to light scattering as particles begin to agglomerate and fall out of solution. Continue adding more methanol until you feel that all of the material has fallen out of solution. Note that this is a judgement call. Adding to little MeOH simply reduces the yield of NPs recovered. Adding too much MeOH, however, may lead to a phase separation with toluene. The resulting suspension is then centrifuged to recover the precipitated NPs.

3.1.7 Ligand exchange

Ligand exchange is accomplished by exposing the NPs to a large excess of the new ligand. We can perform ligand exchange to bring water soluble gold nanoparticles into an organic solvent or vice versa. For simplicity we will do the latter. This means that we will start with our Brust Au NPs and then bring them from toluene into water.

To begin the ligand exchange procedure do the following to a toluene solution of Au NPs. Use 1/4th of the Brust NP solution you made earlier. The solution can be placed in a disposable 50 mL centrifuge tube now since you will later have to centrifuge the mixture. Add 0.1 grams of mercaptoundecanoic acid (MUA) to the NP solution. What is the structure of this compound? Also what side of the molecule will bind to the surface of the NP? What side will eventually stick out in solution and why do you expect this will make the particles water soluble?. On adding MUA you will see that the Au NPs immediately begin to precipitate. Basically your initial toluene solution will start to go cloudy. If you want you can gently heat this suspension to aid the ligand exchange. But this is only optional. In any event, vigorously shake the solution to mix things up well.

Next, you will want to centrifuge the solution to recover your NP precipitate. Centrifuge it at some moderate speed, say 4,000 rpm (actual speed should not matter) for 5 minutes. When you look at the resulting mixture, you will see that the supernatant (toluene mostly) is clear. All of your Au NPs should have precipitated into a nice compact pellet. Discard the toluene supernatant in an appropriate waste container. Now to the precipitate, add 2 mL of tetrahydrofuran, THF. Shake this mixture up well. You will notice that the particles are still not particularly soluble in this solvent. Why? Now add dropwise a commercial 20 weight percent solution of potassium t-butoxide in THF to your THF solution. You will only need less than 0.2 mL of it so its not much. As you add the t-butoxide solution you will see the NPs really start to fall out of solution. There should be big “fluffy” precipitates in solution. Also you will see some white precipitate from the unreacted t-butoxide itself.

After adding the t-butoxide, centrifuge the resulting suspension again for several minutes at 4,000 rpm (actual speed should not matter). The product should consist of a clear THF supernatant and all of your material at the bottom of the tube as a compact colored precipitate. Discard the supernatant. Now finally, add deionized water to your Au NP pellet. The particles should now go into solution. In principle, one can continue this exercise by adding 1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) to conjugate these carboxylic acid terminated Au NPs to amine terminated surfaces. For examples, many proteins have such surfaces. This is therefore a possible project extension for future versions of this laboratory.

For kicks try the following as well. Take another 1/4 of the initial Brust NP solution and crash it out using methanol (i.e. add excess methanol until everything starts falling out of solution). This is basically a repeat of size selective precipitation that we discussed earlier. Now centrifuge the suspension. Discard the clear supernatant and keep the NP precipitate. To the precipitate add water. See if you can bring the particles into solution. You probably can't and you can guess why. This again illustrates the importance of the surface ligands in nanoparticle synthesis. It also illustrates some of the possibilities that one can achieve by exploring the surface chemistry of nanoscale systems.

4 Clean-up

Any gold solutions not needed should be discarded in the appropriate waste container. If the particles are in water they should be placed in an aqueous waste container. Likewise, if the particles are in toleuene, they should be discarded in the organic waste container.

5 Laboratory report points to consider

You should consider the following points in your report.

- How many atoms make up a 10 nm Au NP?
- Consider a 10 nm Au NP. What fraction of atoms do you think reside on the NP surface?
- Based on the amount of precursors used, what is the molarity of the resulting Au NP solution?
- What is the role of the citrate ions in the synthesis?
- Citrate ions are known to reside on the surfaces of the resulting Au NPs. What is their role? Why don't the particles tend to aggregate and fall out of solution?
- What is the role of trioctylphosphine ligands on the NP surface.
- Why is methanol a nonsolvent for TOP passivated Au NPs?

- Why did our ligand exchange make the initially hydophobic NPs hydrophilic?
- How does the light scattering intensity depend on wavelength? This is why the sky is blue. But why do we use red light and not UV light in our light scattering experiments? There are several reasons here.
- How does the light scattering intensity depend on refractive index? What do you think is easier to observe, gold or silica and why?
- How does the light scattering intensity depend on particle size? Do you expect the same size from TEM as from DLS measurements? This is why the measurement is critically dependent on the purity of the water used. Any dust particles prsent may skey your DLS results significantly.
- Do molecules scatter light and would that affect your measurements? Take a blank before your sample to check.

6 Extra TEM images

See attached images at the end of this document.

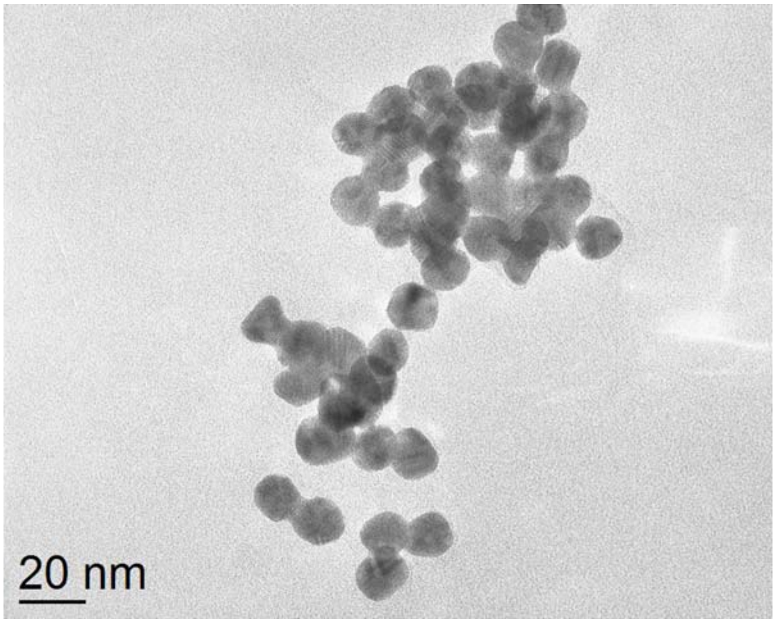

Figure 9: Au NP TEM

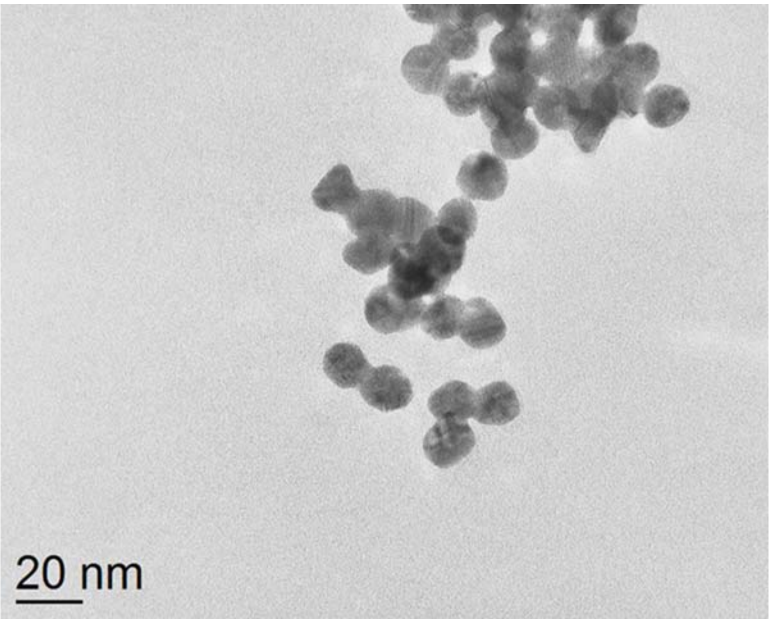

Figure 10: Au NP TEM

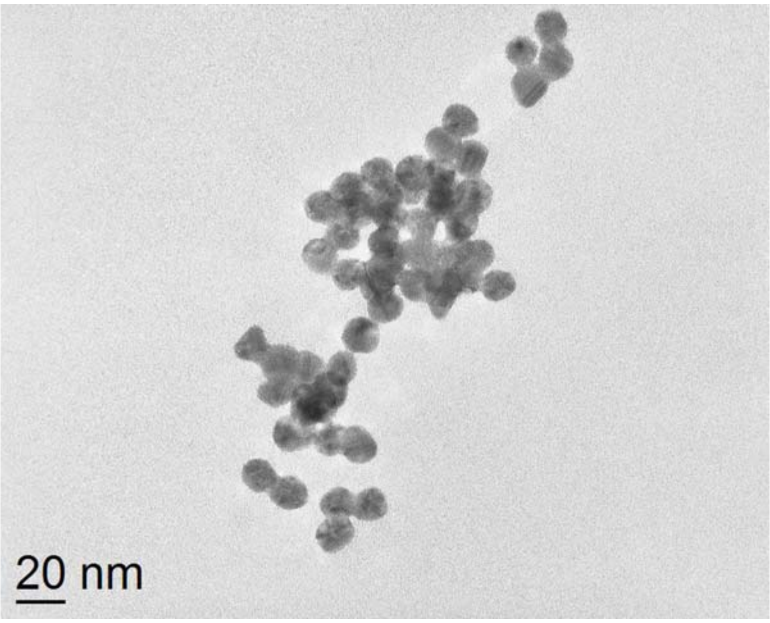

Figure 11: Au NP TEM

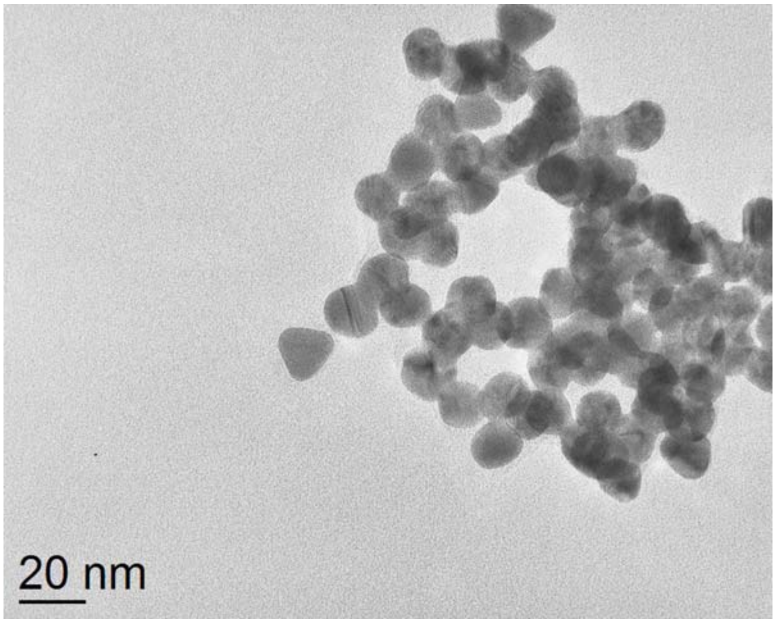

Figure 12: Au NP TEM

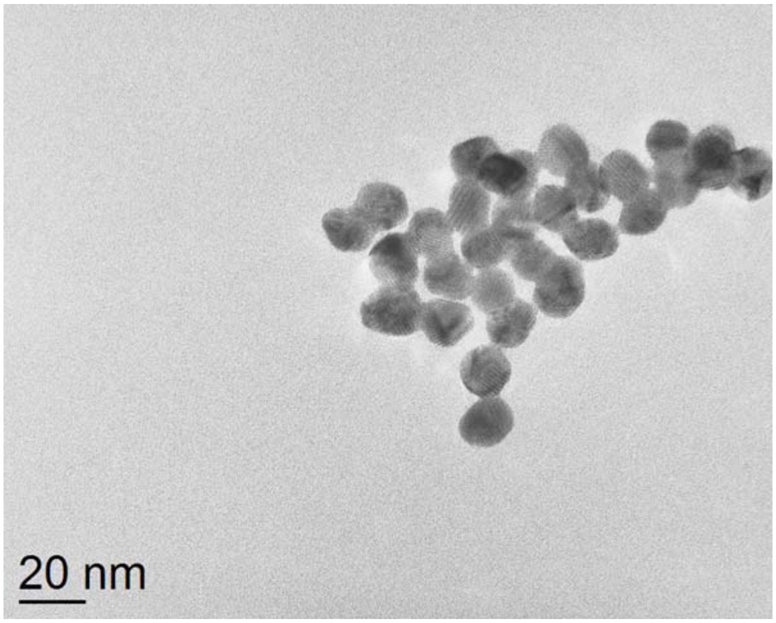

Figure 13: Au NP TEM

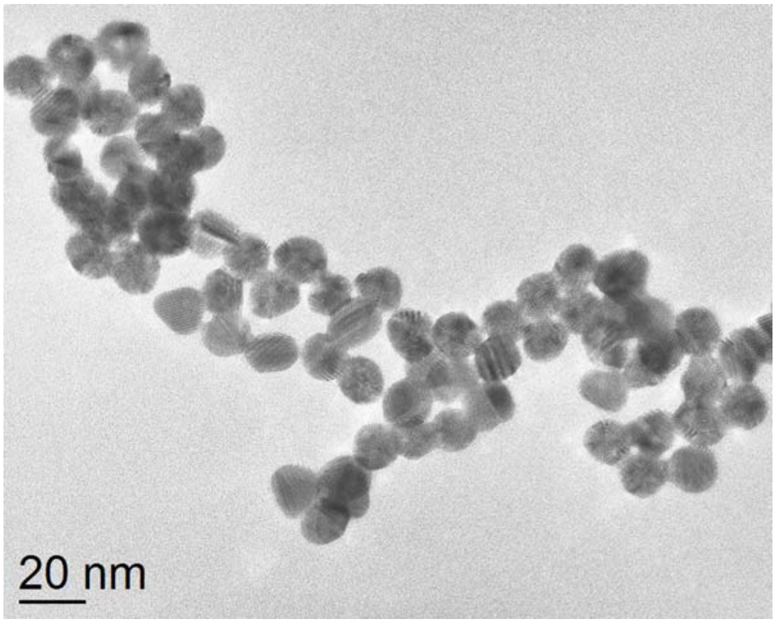

Figure 14: Au NP TEM

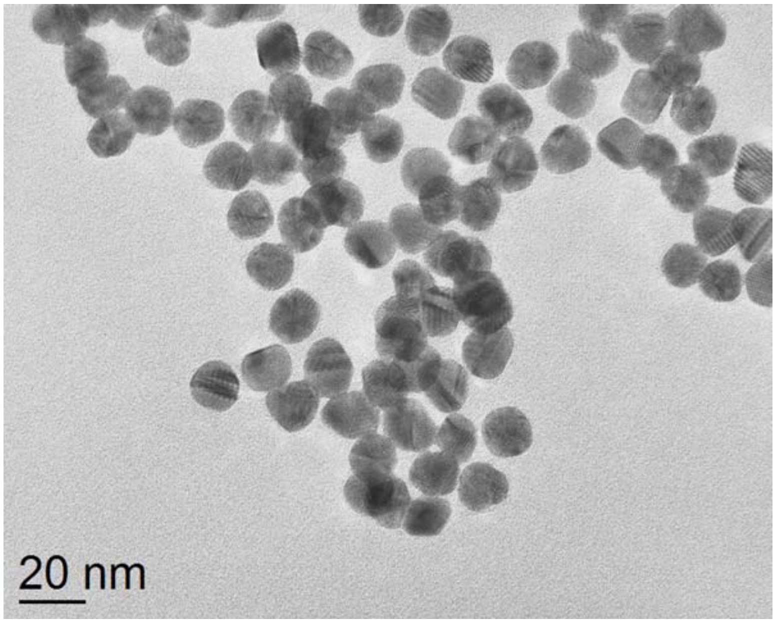

Figure 15: Au NP TEM

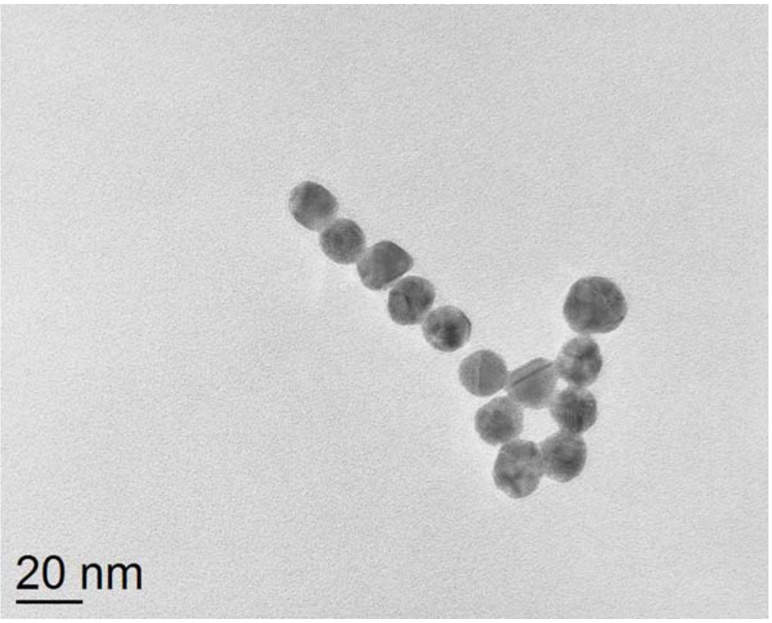

Figure 16: Au NP TEM

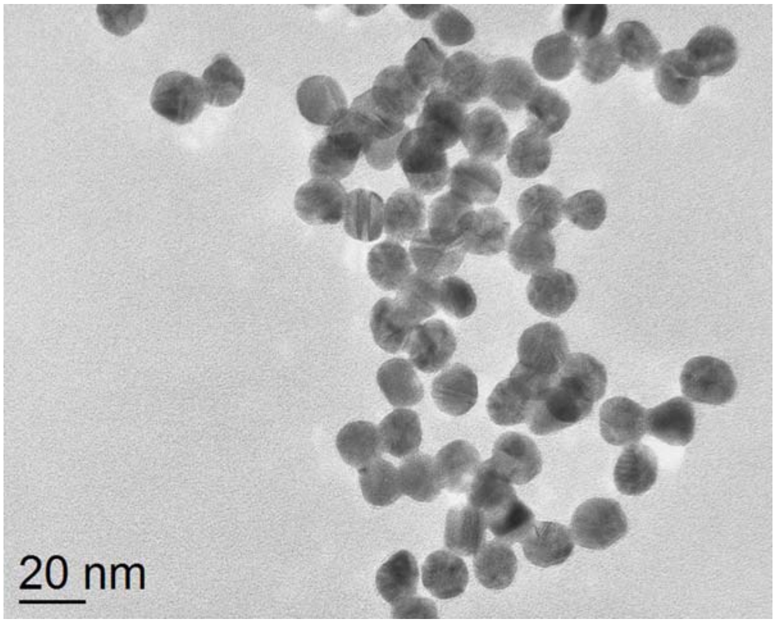

Figure 17: Au NP TEM

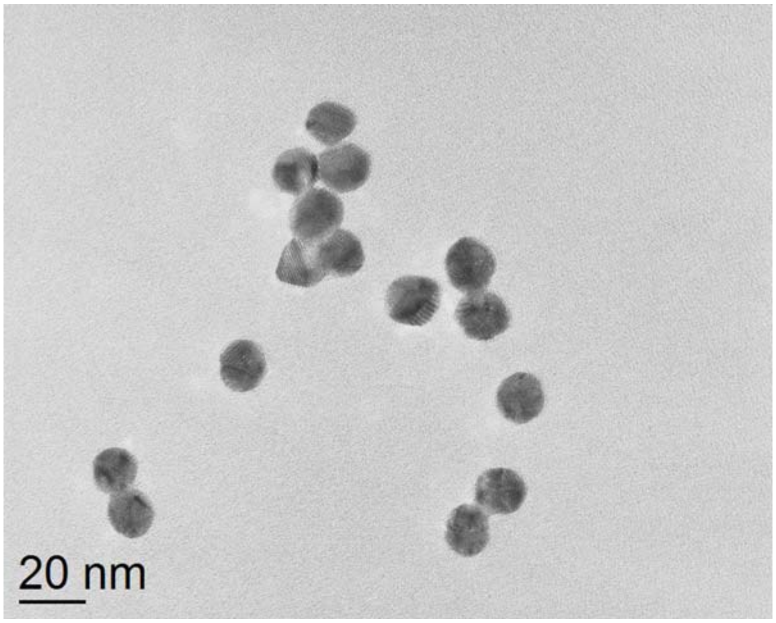

Figure 18: Au NP TEM

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