Synthesis of Noble Metal Nanoparticles

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Dedications

This thesis is dedicated to my incredible parents, Gardooyhe and Manoochar, and to my wonderful husband, Hossein, for their endless support and love, and to my daughters Ava and Ariana for loving me unconditionally.
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Improved methods were developed for the synthesis of noble metal nanoparticles. Laboratory experiments were designed for introducing of nanotechnology into the undergraduate curriculum.

An optimal set of conditions for the synthesis of clear yellow colloidal silver was investigated. Silver nanoparticles were obtained by borohydride reduction of silver nitrate, a method which produces particles with average size of 12±2 nm, determined by Transmission Electron Microscopy (TEM). The plasmon absorbance is at 397 nm and the peak width at half maximum (PWHM) is 70-75 nm. The relationship between aggregation and optical properties was determined along with a method to protect the particles using polyvinylpyrrolidone (PVP). A laboratory experiment was designed in which students synthesize yellow colloidal silver, estimate particle size using visible spectroscopy, and study aggregation effects.

The synthesis of the less stable copper nanoparticles is more difficult because copper nanoparticles are easily oxidized. Four methods were used for the synthesis of copper nanoparticles, including chemical reduction with sodium borohydride, sodium borohydride with potassium iodide, isopropyl alcohol with
cetyltrimethylammonium bormide (CTAB) and reducing sugars. The latter method was also the basis for an undergraduate laboratory experiment. For each reaction, the dependence of stability of the copper nanoparticles on reagent concentrations, additives, relative amounts of reactants, and temperature is explored. Atomic force microscopy (AFM), TEM and UV-Visible Spectroscopy were used to characterize the copper nanoparticles.

A laboratory experiment to produce copper nanoparticles from household chemicals was developed.
Chapter 1: Nanotechnology and Imaging Devices

1.1 Introduction

Matter can be placed into broad categories according to size. Macroscopic matter is visible with the naked eye. Atoms and (most) molecules are microscopic with dimensions < 1nm. Mesoscopic particles, such as bacteria and cells that have dimensions on the order of micron(s), can be observed with optical microscopes. Falling into the gap between the microscopic and the mesoscopic is another class of matter, the nanoscopic particles. The size of nanoparticles is compared to that of other “small” particles in Figure 1.1, where the bacterium is huge in comparison.

Figure 1.1. Size comparisons of “small” particles [1].
Nanotechnology deals with processes that take place on the nanometer scale, that is, from approximately 1 to 100 nm. Nanoscale materials possess unique properties. Advances are occurring in synthesis of isolated nanostructures. This opens the possibility for creating a new generation of advanced materials with designed properties, not just by changing the chemical composition of the components, but by controlling the size and shape of the components. For example, the melting point of nanosized metal particles depends upon the size of the particles. The smaller a particle becomes, the more the proportion of surface atoms increases. As particles decrease in size the number of surface atoms becomes equal to or even exceeds the number of inner-core atoms. For a typical bulk material the surface is negligibly small in comparison to the total volume. Surface atoms are more easily rearranged than those in the center of the particle, and so the melting process, which depends on destroying the order of the crystal lattice, can get started at a lower temperature. The melting point of gold metal is 1064°C. For 11-12 nm gold particles it is about 1000°C, then begins to drop dramatically to 900°C for 5 to 6 nm particles and to 700°C for 2 to 3 nm particles [1].

1.2 Imaging Devices

Bacteria can easily be observed with an optical microscope, but the nanoparticles require far better resolution. Invention of new microscopes has catalyzed rapid advances in the field of nanotechnology. It is now possible to actually see atoms, nanoparticles, and nanoscale materials due to the recent
advances in the imaging technologies such as high resolution transmission electron microscopy (TEM), scanning probe microscopy (SPM), also called scanning tunneling microscopy (STM), atomic force microscopy (AFM), and powder x-ray diffraction (XRD). In the following sections, first limitation of optical microscopes in detection of nanoparticles will be described, and then transmission electron microscopy and atomic force microscopy will be discussed.

1.2.1 Optical Microscopes

Optical systems of any kind that use lenses and mirrors to form an image are limited in their resolution, even with the best designs. The ability to make fine structural details is expressed in terms of numerical aperture (NA). The numerical aperture can be expressed as $n \sin \theta$, where $n$ is the refractive index of the medium between the sample and the objective lens through which the light passes ($n_{\text{air}} = 1.00$; $n_{\text{water}} = 1.33$; $n_{\text{oil}} = 1.4$), and $\theta$ is the acceptance angle of the lens ($\sin \theta = 1$ if the angle is $90^\circ$).

The limits of the objective lens are such that $\theta$ cannot be greater than 90 degrees, and the object space, even if filled with oil, can only reach an NA of 1.4. The resolving power of the light microscope is also limited by the wavelength of the light used for illumination. To explain this more, the resolving power of the optical system can be expressed as:

$$R = \frac{\lambda}{2NA}$$  \hspace{1cm} (1.1)
R is the distance between distinguishable points (in nm), $\lambda$ is the wavelength of the illumination source (in nm), and NA is the numerical aperture of the objective lens.

Reducing the wavelength from red to violet (700 nm to 400 nm) can improve the resolution, as can using an oil immersion lens ($n > 1$), but only so far. The optimal resolving power for a light microscope is obtained with ultraviolet illumination ($\lambda = 365$) if a system with the optimal NA is used (1.4). In this example, R is calculated to be 130.4 nm.

$$R = \frac{365}{2 \times 1.4}, \quad R = 130.4 \text{ nm}$$

Using ultraviolet light is one approach, but it is very expensive. In general, with optical microscopy, even with the best optics, the smallest object that can be measured using visible light is limited to about 500 nm (0.5 micron). Thus, optical microscopy can be used to determine the size of micrometer sized particles (1000 nm, 1 micron), but not nanoparticles (1 to 100 nm) [2].

### 1.2.2 Electron Microscopes

Limitation of resolving power by light microscopy can be modified and applied to the electron microscope by using DeBroglie's formula. In 1924 Louis DeBroglie suggested that the electron had a dual nature, with characteristics of a particle or a wave [3]. The deBroglie wavelength, $\lambda$, for these “matter waves” is:
\[ \lambda = \frac{h}{mv} \]  \hspace{1cm} (1.2)

In the equation, \( h \) is Planck’s constant \((6.63 \times 10^{-34} \text{ J x s})\), \( m \) is the mass of the particle \((9.11 \times 10^{-31} \text{ kg for electrons})\) and \( v \) is the velocity in m/s. The wavelength of electrons in a beam produced from an electron gun can be computed from the accelerating potential, \( V \), and the electron charge, \( e \) \((1.60 \times 10^{-19} \text{ C})\), using the classical expression:

\[ E = V \times e = \frac{1}{2} (mv)^2 \]  \hspace{1cm} (1.3)

Therefore,

\[ v = \left( \frac{2Ve}{m} \right)^{\frac{1}{2}} \]  \hspace{1cm} (1.4)

Substituting into the deBroglie equation and collecting all the constants \((m, e, \text{ and } h)\) for the wavelength gives:

\[ \lambda = 1.23 \frac{nm}{\sqrt{V}} \]  \hspace{1cm} (1.5)

The equation above shows that the wavelength of an electron beam is a function of the accelerating voltage used. By increasing the accelerating voltage, a shorter wavelength is obtained. For an accelerating potential of 1 kV \((1000 \text{ V})\), the wavelength associated with the electrons is 0.0388 nm, compared to the wavelength of violet light, about 400 nm. The shorter the wavelength the smaller
is the limit of resolution of the microscope. Using such waves in a microscope results in a significant increase in resolution [4].

In the electron microscope accelerated electrons strike the object to be examined. Images are formed because the thicker portions of the sample absorb more of the electron stream than the thinner portions.

1.2.2.1 Transmission Electron Microscope

The transmission electron microscope (TEM) was the first type of electron microscope to be developed and is patterned exactly on the light transmission microscope except that a focused beam of electrons is used instead of light to “see through” the specimen. A more technical explanation of typical of how TEMs work is as follows (Figure 1.2) [5, 6]:

1. The electron gun at the top produces a stream of monochromatic electrons.
2. The double condenser lenses focus the electron beam onto the specimen.
3. The beam is constrained by the condenser aperture taking out high angle electrons (those far from the optic axis).
4. The electron beam strikes the sample, depending on the density of the material present, some of the electrons are scattered and disappear from the beam and parts of it are transmitted.
5. This transmitted portion is focused by the objective lens into an image.
6. Unfocussed electrons are blocked out by the objective aperture, resulting in an enhancement of the image contrast.

7. The image is passed down the column through the intermediate and projector lenses, and becomes enlarged.

8. At the bottom of the microscope the unscattered electrons hit the phosphor image screen, and light is produced, allowing the user to see a “shadow image” of the specimen with its different parts displayed in varied darkness according to their density. The darker areas of the image represent those areas of the sample that fewer electrons were transmitted through which are thicker or denser areas. The lighter areas of the image represent those areas of the sample that more electrons were transmitted through (they are thinner or less dense), Figure 1.3 shows a TEM image of copper nanoparticles. Although the electron microscope is an improvement over the optical microscope, the image it produces is two-dimensional.
Figure 1.2. Typical TEM functioning [7].

Figure 1.3. TEM image of Cu nanoparticles. The copper nanoparticles were prepared in our lab.
1.2.3 Scanning Probe Microscopes

Since the 1980’s lab researchers and companies have developed several types of scanning probe microscopes (SPMs) to see and to manipulate atoms and molecules. The SPMs are able to image an object’s surface in three dimensions. They provide nanometer-scale resolution by using a sharp tip, the probe, which touches or nearly touches a sample’s surface to create images or measure the properties of materials (See Section 1.2.2.1). SPMs include the scanning tunneling microscope (STM) and the atomic force microscope (AFM). The first scanning probe microscope was the scanning tunneling microscope.

In STM, the structure of a surface is studied using a probe that scans the surface at a fixed distance from it. The electron cloud associated with metal atoms at a surface extends a very small distance above the surface. When an extremely fine conducting probe is held close to the sample, there is a strong interaction between the electron cloud on the surface and that of the tip and an electric tunneling current flow between them. At a separation of a few atomic diameters, the tunneling current rapidly increases as the distance between the tip and the surface decreases. This rapid change of tunneling current with distance results in atomic resolution when the tip is scanned over the surface and an image is produced. For STM, good resolution is considered to be 0.1 nm lateral resolution and 0.01 nm depth resolution. One disadvantage of the STM technique is its restriction to electrically conducting surfaces [8]. A further development of
the STM, atomic force microscope, will be discussed in detail here, since it was used for characterization of copper nanoparticles.

1.2.3.1 Atomic Force Microscope (AFM)

The atomic force microscope (AFM) has a broader range of capabilities than the STM. The AFM can be used to investigate any surface, even poorly or nonconductive ones, which broadens its potential applications significantly [9]. The instrument measures forces on a surface by scanning the sample with the tip attached to a flexible cantilever. The resolution obtained by AFM is determined in large part by the size of the probe tip used for imaging. Pyramidal or needle shaped silicon (Si) or silicon nitride (Si₃N₄) are the two main tips used in AFM. These probes have end radii of curvature as small as 10 nm but are often much larger [10, 11]. Advances are always being made to create a better tip [12], for example, SuperSharpSilicon™ tips are offering radii of typically 2 nm [13].

The way the AFM operates is similar to the principle behind the record player in that the tip moves up and down in response to the surface features. An optical readout, or a piezoelectric crystal, translates the motion of the cantilever into an electronic signal. The outcome is a three-dimensional image of the surface structure displayed on a screen. Maximum resolution is typically on the atomic scale in the lateral and vertical directions.
The way in which image contrast is obtained in AFM can be achieved in many ways [9, 11, 14]. The three main classes of interactions are contact mode, non-contact mode and tapping mode.

i. Contact mode, also known as repulsive mode, is the common method used in the AFM. The tip and sample remain in close contact while the scanning proceeds. The tip is attached to the end of a cantilever with a low spring constant, holding the atoms of the sample together. In AFM the repulsive van der Waals force balances almost any force that attempts to push the tip and sample closer together. When the cantilever pushes the tip against the sample, it bends rather than forcing the tip atoms closer to the sample atoms, thus accommodates changes in topography (Figure 1.4). One of the problems of remaining in contact with the sample is caused by excessive tracking forces applied by the probe to the sample, which can damage the sample and distort image data. An effort to avoid this problem is to use the non-contact mode.

ii. A new era in imaging was opened when non-contact mode was introduced, and it is used in situations where tip contact might alter the sample. In non-contact mode the cantilever is oscillated in the attractive regime, meaning that the tip is quite close to the sample, but not touching it (Figure 1.4). Attractive Van der Waals forces acting between the tip and the sample are detected, the tip scans above the surface and topographic images are created. Non-contact imaging generally provides low resolution, and it is a very difficult mode to
operate with the AFM. The thin layer of water contamination that may exist on
the surface of the sample will form a small capillary bridge between the tip and
the sample and cause the tip to jump-to-contact.

iii. Instead, the tapping mode can be used. This technique allows users to
obtain high resolution topographic imaging of sample surfaces that are easily
damaged, poorly immobilized, or difficult to image by other AFM techniques.
Tapping mode improves the AFM functionality by placing the tip in contact with
the surface to provide high resolution and then lifting the tip off the surface to
avoid dragging the tip across the surface (Figure 1.4). In this mode, the cantilever
is oscillated at its resonant frequency (50 to 500 kHz) and positioned above the
surface so that it only taps the surface for a very short time. When the oscillating
cantilever begins to contact the surface, the cantilever oscillation is unavoidably
reduced. The reduction in oscillation amplitude is used to identify and measure
surface features.

The advantage of the tapping mode technique is that it prevents the tip
from sticking to the surface and causing damage during scanning. Another
advantage of this technique is that the surface material is not pulled sideways by
shear forces since the applied force is always vertical.

One of the disadvantages of the tapping mode is that the tip-sample impact
force in this mode is so great that it is destructive. The tip-sample impact force is
greater than in typical contact mode AFM. This force results in significant tip wear, which limits the resolution, and can damage the sample. This is even more so a problem in the case of imaging soft materials.

**Figure 1.4.** Non-contact mode (top), contact mode (middle), and tapping mode (bottom) [15].
1.2.3.2 EasyScan DFM

The easyScan dynamic force microscope (DFM) is an atomic force microscope that can be used in both static and dynamic operating modes [16-18]. Dynamic force mode can also be called tapping mode, intermittent contact mode, wave mode, by various AFM manufacturers. The static force operating mode is the contact mode. In dynamic force mode instead of tracing the surface line by line with a constant force, the cantilever vibrates near its resonance frequency and scans across the surface with constant vibration amplitude, thus experiencing only intermittent contact with the surface. The cantilever vibration amplitude can now be used as an input for a feedback loop that keeps the tip sample interaction constant by changing the tip height. When the tip passes over a bump in the surface, the cantilever has less room to oscillate and the amplitude of oscillation decreases. On the contrary, when the tip passes over a depression, the cantilever has more room to oscillate and the amplitude increases. The output of this feedback loop thus corresponds to the local sample height. An image of the surface is made by recording the sample height as the tip is scanned over the sample surface in the x and y direction (Figure 1.5). The plot of z-value representing particle height is displayed in the “line view” window and the particle size is defined as the maximum height of the particle, as it is shown in Figure 1.6a. The particle may be visualized in a two dimensional (Figure 1.6b), or a three dimensional format (Figure 1.6c).
Figure 1.5. DFM system: computer, cantilever with the measurement system scanning the sample [19].

The DFM can be used to measure the topography and several other properties of a sample with nanometer resolution. Dynamic force mode has an advantage over contact mode in the sense that it will damage the sample less since there is no drag force to pull the sample sideways. However, the tip-sample impact force in the DFM mode is huge, results in significant tip wear and can damage the sample (See Section 1.2.2.1, tapping mode). One solution to this problem is frequent replacing of the tip.
Figure 1.6. AFM scan results of Cu nanoparticles in mica surface, a) one dimensional plot of z-value representing height of one particle, b) two dimensional, and c) a three-dimensional view of particles in a 10.3 μm x 10.3 μm scan area.
Operation of the easyScan DFM is simple, and minimal setup is required. EasyScan DFM offers a compact, mobile design, the AFM and control electronics fit inside a single briefcase. Use of a laptop computer allows users to take the entire system wherever they want (Figure 1.7). The stand-alone design allows the AFM to be placed on any surface to image. The easyScan has a much lower price than other AFMs without giving up quality or support [20]. For the above reasons easyScan DFM is highly desirable for educational purposes and has been adopted in many institutions; such as the University of Virginia, University of Washington, and Juniata College.

Figure 1.7. EasyScan DFM [20].
1.3 Comparison of Atomic Force Microscope and Transmission Electron Microscope

AFM can be performed in liquid or gas medium. Liquid dispersions of particles can be scanned, provided the dispersant is not corrosive to the probe tip. In contrast TEM generally requires high vacuum conditions, which can alter the particles being examined. For example, with combustion-generated nanoparticles, major components of the particles are volatile components that evaporate at low pressure. Compared with TEM, three dimensional AFM images are obtained without expensive sample preparation and yield far more complete information than the two-dimensional profiles available from cross-sectioned samples [21-23].

For several reasons, TEM by far is the best technique available for size determination of nanoparticles, because it combines very high resolution (subnanometer) at the highest magnifications along with a very wide field of view at lower magnifications [24, 25]. For example, operation at magnification of x 100,000 yields very sharp images with a field of view incorporating hundreds of 12 nm diameter gold particles (Figure 1.8). This accuracy in measurement of diameter allows for a number sufficient for a statistically significant determination of particle diameter. In contrast, AFM is widely applicable but yields data that are the least straightforward to interpret. For example, often the size of features on the surface such as nanospheres looks larger than expected. The reason is that images measured with an atomic force microscope are always a convolution of the probe geometry, which is explained in detail in section 1.3.1.
1.3.1. Probe Artifact

One of the most important factors influencing the resolution of an AFM is the sharpness of the scanning tip. The best tips may have a radius of curvature of only around 5 nm. The need for sharp tips is normally explained in terms of tip convolution, which means any influence the tip may have on the image, such as broadening. If the radius of curvature of the tip is comparable to or greater than the size of a sphere particle attached to a surface, the side of the probe will cause a broadening of features in the image as it scans over the specimen. In this motion the sides of the tip make contact before the apex, and the microscope begins to respond to the feature. This creates the image distortion called a “convolution” of the tip. However, the height of the feature when measured by a line profile (z-value) is correct [9-11, 26]. Figure 1.9 shows motion of an AFM probe scanning over a sphere that is attached to a surface. The AFM line profile of the
nanoparticle demonstrates that the width of the nanoparticle depends on probe shape; however, the nanoparticle height is independent of the probe shape. This fact is not a function of particle size but rather an intrinsic property of AFM.

It is important to know if the probe is much smaller than the feature to be imaged; then the probe-generated artifacts will be minimal and the dimensional measurements will be accurate.

**Figure 1.9.** a) The probe tip diameter is much smaller than the diameter of the particle, b) the probe tip is much larger than the particle [27].

Convolution of finite tip size can be seen in Figure 1.10, the surface was derivatized with spherical 12 nm diameter gold particles, but each particle appears to have an in-plane (XY) dimension of about 35 nm, and thus the particle size appears larger than the calculated value. However, measurements of particle height by AFM correspond reasonably well with values (diameter of particles) measured by TEM [25, 26]. This can easily be seen in copper nanoparticles prepared in our lab and characterized by both an atomic force microscope, easyScan DFM, (Figure 1.11) and by a TEM (Figure 1.12). The mean diameter of
copper particles measured by TEM is 18 nm and maximum height measured by AFM is 20 nm.

Figure 1.10. 500 × 500 nm AFM image of 12 nm colloid Au particles, the particles appear about 35 nm in XY plane [25].
Figure 1.11. a) (5.39 µm x 5.39 µm) AFM image of Cu nanoparticles, b) size distribution of colloidal Cu dispersion (20±2 nm the height of the particle). The Cu nanoparticles were prepared in our lab.

Figure 1.12. a) The TEM image of Cu NPs (The size bar is 20 nm), b) size distribution, and the diameter of the particle for this sample is 18±2 nm. The Cu nanoparticles were prepared in our lab.
1.4 Nanotechnology in Education

Portable and relatively inexpensive STMs ($8000) and AFMs ($24,000) can be purchased for educational use.

A course was developed in 2007 at the University of Virginia under NSF and UVA funding. It provides an introduction to the world of nanoscience. The course is intended for freshman and sophomores of all disciplines. It exploits new generation miniaturized instrumentation, including easyScan STM and easyScan AFM. Also, in UVA a Virtual Lab (UVA Virtual Lab©) that uses 3D animation to disassemble and examine complex instrumentation such as atomic force microscopes and scanning tunneling microscopes has been developed. Over 50 educational VR animations can be viewed at the UVA Virtual Lab© [28].

Currently, the Nanobiotechnology Center (NBTC) at Cornell University hosts hands-on science activities for interested teachers and students in grades K-12. In addition, a graduate-level course, nanobiotechnology, was offered at Cornell University in 2007 [29]. Other institutions, including North Carolina State University, University of North Carolina, Rice University and Virginia Tech, Pennsylvania State University offer programs for the general public, K-12, college students, and teachers.
At Juniata College a laboratory experiment to use easyscan-DFM for characterization of gold nanoparticles was developed. In this experiment students prepare colloidal gold, then use visible spectroscopy and easyscan-DFM to characterize the gold nanoparticles. Students learn to use the esayscan DFM, which is easy to operate, and they learn to measure the particle size and distribution [30]. This work was the result of collaboration between Juniata College and Drexel University. The experiment for synthesis of gold nanoparticles was developed by Dr. Solomon’s group at Drexel University, chemistry department and characterization of colloidal gold by DFM was done at Juniata College.

In our laboratory an experiment on the synthesis of silver nanoparticles has been designed which was published in the Journal of Chemical Education [31], and is currently part of the laboratory curriculum at Drexel University (Appendix A). The experiment developed by our group has also been made available nationwide through the Interdisciplinary Education Group on a website established at the University of Wisconsin – Madison. They create new instructional materials based on current advances in nanoscale science and technology through the: development and dissemination of kits, creation and dissemination of in depth, high-visual content, video lab, and so on. The synthesis of silver nanoparticles was posted in the video lab section [32]. In addition, this experiment is performed by advanced high school classes through the “Science in Motion Outreach Program” (Science in Motion is a program that
transports equipment and expertise as requested by teachers in Pennsylvania public schools). Furthermore, an experiment on the synthesis of copper nanoparticles using household chemicals has been designed in our laboratory, which will be tested at Drexel University (Appendix B).
References


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Chapter 2: Noble Metal Nanoparticles

2.1 Introduction

The striking effect of nanoparticles on color has been known since antiquity when tiny metal particles were used to color glass in church windows. Silver particles stained the glass yellow, while gold and copper particles were used to make ruby glass [1]. However the nature of these colloids remained unclear, until Faraday explained how metal particles affect the color of church windows [2]. He demonstrated the preparation of gold colloids by reducing an aqueous solution of gold chloride with phosphorus. His samples displayed a stable, ruby-red color, and some of them are still preserved today in the Faraday Museum in London. Nowadays numerous additional procedures exist for the preparation of noble metal colloids.

2.1.1 Terminology

As the field of nanostructured materials has evolved, many terms have been used, including the ones discussed below.

_Nanoparticle:_ A nanoparticle (NP) has dimensions in the nanometer range, e.g. between 0.5 and 100 nm.

_Nanocrystal:_ Nanocrystal is a solid particle that is a single crystal in the nanometer size range.
**Nanostructured or nanoscale materials:** A nanoscale material is any solid material that has a nanometer dimension; such as three dimension (particles); two dimensions (thin films); one dimension (thin wire).

**Colloids:** Solutions can contain particles ranging in size from 0.1 to 10 nm. In colloids the particle size ranges from about 10 to 100 nm. Colloidal particles may consist of single units or groups of them. A 14-nm nanoparticle of gold, for instance, contains about 50,000 atoms [3]. Components of colloids are assigned general names which are analogous to the solution terms: solute (the dispersed medium) and solvent (the dispersing medium or continuous phase). Colloids may form from any combination of liquid, solid or gas, except for gas and gas. Gases always dissolve in each other to form true solutions. Colloidal dispersions of insoluble materials are called sols. Examples of “sols” are the red colloidal gold and the yellow colloidal silver nanoparticles. Common colloids are listed in Table 2.1.
Table 2.1. Types of colloids.

<table>
<thead>
<tr>
<th>Disperse phase</th>
<th>Continuous phase</th>
<th>Names</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>Gas</td>
<td>Aerosols: fog, mist</td>
</tr>
<tr>
<td>Solid</td>
<td>Gas</td>
<td>Aerosols: smoke</td>
</tr>
<tr>
<td>Gas</td>
<td>Liquid</td>
<td>Foams; whipped cream</td>
</tr>
<tr>
<td>Liquid</td>
<td>Liquid</td>
<td>Emulsions: mayonnaise, milk</td>
</tr>
<tr>
<td>Solid</td>
<td>Liquid</td>
<td>Sol: colloidal gold</td>
</tr>
<tr>
<td>Liquid</td>
<td>Solid</td>
<td>Gels: jellies</td>
</tr>
</tbody>
</table>

2.2 Size of Metal Nanoparticles

Properties of metal nanoparticles, which contain less than one million atoms, are different from those of bulk materials made from the same atoms.

2.2.1 Magic Numbers

About 70% of the elements are metals. Many of these have face-centered cubic (FCC) crystal structures. Each atom in this close-packed structure is surrounded by 12 other atoms. Figure 2.1a shows the 12 neighbors that surrounded an atom located in the center of a cube for a FCC lattice and Figure 2.1b presents another perspective of the 12 nearest neighbors. These 13 atoms represent the smallest theoretical nanoparticle for a FCC lattice. Figure 2.1c shows the 14-sided polyhedron called cuboctahedron, which maintains the FCC geometry. The three open circles at the upper left of Figure 2.1c are the three atoms on the top layer of Figure 2.1b, the six solid circles plus the atom (not
pictured) in the center of the cube of Figure 2.1c represent the middle layer of that figure, and the open circle at the lower right of Figure 2.1c is one of the three atoms (not shown) at the bottom of the cluster of Figure 2.1b. This 14-sided polyhedron has six square faces and eight equilateral triangle faces. If another layer of 42 atoms is laid down around the 13-atom nanoparticle, a 55-atom nanoparticle with the same cuboctahedron shape is formed (Figure 2.1d).

The smaller a particle becomes, the more the proportion of surface atoms increases. For bulk materials the surface atoms form a negligible fraction of the total number of atoms. Table 2.2 gives the number of atoms in FCC metal nanoparticles including the number on the surface and the diameter of each particle (including diameters for gold nanocrystals). The total number of atoms in particles, 1, 13, 55, 147, … , are called “structural magic numbers” [3-5]. For $n$ layers the number of atoms $N$ in this FCC nanoparticle is given by the formula:

$$N = \frac{1}{3} \left(10n^3 - 15n^2 + 11n - 3\right)$$

and the number of atoms on the surface $N_{\text{surf}}$ is

$$n_{\text{surf}} = 10n^2 - 20n + 12$$

The diameter of each nanoparticle is given by the expression $(2n-1)d$, where $d$ is the distance between the centers of the nearest–neighbor atoms, and

$$d = \frac{\alpha}{\sqrt{2}}, \text{ where } \alpha \text{ is the lattice constant (length of the edge of the unit cell).}$$
Figure 2.1. a) FCC unit cell, b) a closed packed Au13 cluster, c) cuboctahedron geometry of Au13 [5], d) cuboctahedron geometry of Au55.

Table 2.2. The relationship between the diameter (d) of the gold particle, the total number of the atoms and the percentage of surface atoms [5].

<table>
<thead>
<tr>
<th>Shell</th>
<th>Number of diameters</th>
<th>d, Au nm</th>
<th>Total atoms</th>
<th>Surface atoms</th>
<th>% Surface atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1d</td>
<td>0.288</td>
<td>1</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>3d</td>
<td>0.864</td>
<td>13</td>
<td>12</td>
<td>92.3</td>
</tr>
<tr>
<td>3</td>
<td>5d</td>
<td>1.44</td>
<td>55</td>
<td>42</td>
<td>76.4</td>
</tr>
<tr>
<td>4</td>
<td>7d</td>
<td>2.01</td>
<td>147</td>
<td>92</td>
<td>62.6</td>
</tr>
<tr>
<td>5</td>
<td>9d</td>
<td>2.59</td>
<td>309</td>
<td>162</td>
<td>52.4</td>
</tr>
<tr>
<td>6</td>
<td>11d</td>
<td>3.16</td>
<td>561</td>
<td>252</td>
<td>44.9</td>
</tr>
<tr>
<td>7</td>
<td>13d</td>
<td>3.74</td>
<td>923</td>
<td>362</td>
<td>39.2</td>
</tr>
<tr>
<td>8</td>
<td>15d</td>
<td>4.32</td>
<td>1415</td>
<td>492</td>
<td>34.8</td>
</tr>
<tr>
<td>9</td>
<td>17d</td>
<td>4.89</td>
<td>2057</td>
<td>642</td>
<td>31.2</td>
</tr>
<tr>
<td>10</td>
<td>19d</td>
<td>5.47</td>
<td>2869</td>
<td>812</td>
<td>28.3</td>
</tr>
<tr>
<td>25</td>
<td>49d</td>
<td>14.1</td>
<td>$4.9 \times 10^4$</td>
<td>5083</td>
<td>23.8</td>
</tr>
<tr>
<td>50</td>
<td>99d</td>
<td>28.5</td>
<td>$4.04 \times 10^5$</td>
<td>$2.40 \times 10^4$</td>
<td>5.9</td>
</tr>
<tr>
<td>100</td>
<td>199d</td>
<td>57.3</td>
<td>$3.28 \times 10^6$</td>
<td>$9.80 \times 10^4$</td>
<td>3.0</td>
</tr>
</tbody>
</table>

*Diameter of a gold atom is 0.288 nm.*
As can be seen in Table 2.2, the fraction of surface atoms increases dramatically with decreasing particle size. A nanoparticle of 3 nm would have ~45% of the atoms on the surface, compared to ~76% for a 1 nm particle.

Properties, such as reactivity and melting temperature have all been observed to change when particles become smaller than a critical size. Gold clusters with more than 1000 atoms have the same melting point as bulk gold. As the number of atoms decreases along with the size of the gold particles, the melting point goes down as discussed in Chapter 1 (Section 1.1). In heterogeneous catalysis, for example, it is well known that the increasing proportion of surface atoms with decreasing particle size (Table 2.2) makes small metal particles highly reactive. How the size of a metal nanoparticle affects color is discussed next.

2.3 Optical properties

Copper and gold are the only metals that are colored. The others appear silvery when smooth caused by total reflection of light. All finely divided metals (including gold and copper) are dark brown to black due to total absorption of light by the large surface.

The influence of nanoparticles on color has been known since antiquity. The distinctive colors of colloidal gold, silver and copper are due to a fact known
as plasmon absorbance. Incident light creates oscillations in conduction electrons on the surface of the nanoparticles and electromagnetic radiation is absorbed.

**Surface Plasmons**

Many metals (e.g., alkali metals, Mg, Al, and noble metals such as Au, Ag, and Cu) can be treated as free-electron systems. Such a metal called a plasma, contains equal numbers of positive ions (fixed in position) and conduction electrons (free and highly mobile). Under the irradiation of an electromagnetic wave, the free electrons are driven by the electric field to oscillate coherently at a plasma frequency of $\omega_p$ relative to positive ions [6] (See Section 2.3.3, equation 2.4). Quantized plasma oscillations or collective oscillations of the free electrons are called plasmons. An electromagnetic wave imposing on a metal surface only has a certain penetration depth (<50 nm for Ag and Au), thus just the electrons on the surface are the most significant and their collective oscillations are termed surface plasmons (SPs). These plasmons can interact, under certain conditions, with visible light in a phenomenon called surface plasmon resonance (SPR) [7-9]. An example of this interaction between light and electrons of a metal particle is illustrated in Figure 2.2. For this phenomenon to happen, the particle must be much smaller than the wavelength of incident light. The electric field of incident light can induce an electric dipole in the metal particle by displacing many of the delocalized electrons in one direction away from the rest of the metal particle and thus producing a net negative charge.
on one side. The side opposite the negative charge has a net positive charge (nuclei).

Figure 2.2. Schematic illustration of the collective oscillation of free electrons under the effect of an electromagnetic wave [6].

2.3.2 Calculation of Plasmon Band

The Drude model and Mie Theory are used to describe the surface plasmon band and the factors that determine its position, intensity and broadness [10, 11].

The interactions of light with spherical metal particles can be described by Mie theory. This theory also predicts what fraction of light imposing upon colloidal metal particles will be absorbed and what fraction will be scattered. The sum of absorption and scattering is the extinction of light, which is known as surface plasmon band (SPB) or plasmon absorbance.

The expression for the extinction cross section $C_{ext}$, is:
\[ C_{\text{ext}} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \times \frac{\varepsilon''}{(\varepsilon' + 2\varepsilon_m)^2 + \varepsilon''^2} \]  

(2.1)

The particle radius is \( R \), and \( \varepsilon_m \) is the dielectric constant of the medium. For free electrons, the dielectric function in terms of frequency (\( \omega \)) is described by the Drude model:

\[
\varepsilon' = \varepsilon'' - \frac{\omega_p^2}{(\omega^2 + \omega_d^2)}
\]  

(2.2)

and

\[
\varepsilon'' = \frac{\omega_p^2 \omega_d}{\omega(\omega^2 + \omega_d^2)}
\]  

(2.3)

The bulk plasmon frequency, \( \omega_p \) (for a bulk metal with infinite size), is:

\[
\omega_p = \left( \frac{Ne^2}{\varepsilon_0 m_e} \right)^{1/2}
\]  

(2.4)

where \( N \) is the number density of electrons, \( \varepsilon_0, 8.85 \times 10^{-12} \text{ C}^2/\text{Jm} \), is the dielectric constant of a vacuum, and \( e \) and \( m_e \) are the charge and effective mass of an electron, respectively. The calculated value of the surface plasmon resonance for gold, which has a number density of \( 5.90 \times 10^{28} \text{ m}^{-3} \), is \( 1.37 \times 10^{16} \text{ s}^{-1} \) (9.0 eV).

The quantity \( \omega_d \) is the damping frequency, which depends upon particle size and increases when the particle size decreases.

Substituting expressions for \( \varepsilon' \) and \( \varepsilon'' \) into equation (2.1) in terms of \( \lambda \) gives:
The intensity of the surface plasmon absorbance as well as its position and bandwidth depend on particle size. From the equation above it is clear that the intensity depends on R, the diameter of the nanoparticle. The position and bandwidth also depend on size, but indirectly, through the dielectric constant $\varepsilon$, which includes $\omega_d$, the size-dependent damping frequency. The damping frequency, $\omega_d$, increases as particle size decreases. As the damping frequency increases, the plasmon band broadens as seen in the plots of $Q_{ext}$ ($C_{ext}/\pi R^2$) vs. wavelength for a typical metal particle (Figure 2.3).
Figure 2.3. Plot of $Q_{\text{ext}}$ vs wavelength for a noble metal nanoparticle. Solid line: $\omega_d = 1.4 \times 10^{14} \text{ s}^{-1}$, dashed line: $\omega_d = 5.6 \times 10^{14} \text{ s}^{-1}$.

2.3.3 Experimental Results for Plasmon Band

The position, the shape and intensity of the SPB strongly depend on various factors including the size, shape and monodispersity of the NPs, as well as the composition of the surrounding media and interactions between stabilizing ligands and the NPs [12-15].

2.3.3.1 Size of Particles

Figure 2.4 shows the experimental results for SPB for spherical gold colloids with varying diameters. As can be seen in Figure 2.4, as the particle size increases, the plasmon band frequency decreases or shifts to longer wavelengths.

For small particles, such as gold particles with diameter less than 20 nm,
extinction of light is primarily due to absorption; larger particles tend to demonstrate much stronger scattering [16].

For copper nanoparticles, as the size of nanoparticles increases, the intensity of the band also increases [13, 14]. Figure 2.5 shows absorption spectra of spherical copper metallic particles ranging in size from 1 to 20 nm. A progressive appearance in the 558 nm plasmon peak occurs upon increasing the size of copper particles. It is clear that copper particles with diameters below 4 nm are characterized by strong broadening of the plasmon resonance and SPR is not observed for particles 1 to 2 nm [15].

Figure 2.4. Plasmon band of 22 nm, 48 nm, and 99 nm spherical Au particles [16].
Figure 2.5. Absorption spectra of spherical copper NPs with their sizes [15].

2.3.3.2 Shape of Particles

Particles of different shapes have different plasmon properties [14, 17, 18]. For example, the absorption spectrum of 10 nm spherical copper particles, produced via the reduction of copper dodecyl sulfate (Cu(DS)₂) by sodium borohydride, is characterized by plasmon peak centered at 558 nm (Figure 2.6). The maximum of absorption spectrum for elongated particles is centered at 564 nm, while for interconnected network of copper particles; the maximum is centered at 570 nm. Figure 2.6 illustrates the red shift in the plasmon peak when the shape of the copper particles changes from spheres to rods [14].
2.3.3.3 Aggregation of Particles

Aggregation of colloidal metal particles can also lower their plasmon frequencies and shifts the plasmon absorbance to longer wavelengths [7]. For example, the characteristic plasmon absorbance of silver nanoparticles (10-14 nm) produced in water is near 400 nm. Due to aggregation of silver nanoparticles a new broad peak around 525 nm appears along with a decrease in the intensity of the plasmon absorbance (See Section 3.4.5 and Figure 3.10) [19].

2.3.3.4 Medium Surrounding the Metal Particles

The refractive index of the medium surrounding the metal particles can influence the frequency of their SPBs [7, 9, 12]. Typically, a higher refractive index of the medium produces a lower plasmon frequency. Assuming that an oscillating weighted spring represents the electric field of the SP and a high
dielectric medium to represent a viscous medium like oil, then a spring in a vacuum will oscillate with a higher frequency than the spring in the oil.

### 2.4 Preparation of Noble Metal Nanoparticles

Many techniques, including chemical and physical means, have been developed to prepare metal nanoparticles, such as chemical reduction using a reducing agent [20-25], electrochemical reduction [26, 27], photochemical reduction [28-29], and heat evaporation (including chemical vapor deposition) [30-32]. Nanoparticles can be made by evaporating atoms from the surface of a metal by using a high energy laser, then cooling them into nanoparticles (a physical method).

Physical ways usually need a high temperature (over 1000 °C), vacuum and expensive equipments. There are also easy and convenient chemical methods that use dilute aqueous solutions and simple equipment.

#### 2.4.1 Reducing Agents

In general, the chemical reduction reactions involve reducing agents that are reacted with a salt of the metal according to the following chemical equation:

\[
mMe^{n+} + nRed \rightarrow mMe^0 + nOx
\]

Table 2.3 gives a list of reagents most commonly used in the reduction of gold, silver, and copper salts along with the appropriate conditions. Brief
description of chemical methods to prepare gold, silver and copper nanoparticles are described.

<table>
<thead>
<tr>
<th>Metal species</th>
<th>E°/V</th>
<th>Reducing agent</th>
<th>Conditions</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>≥ + 0.7</td>
<td>Alcohol, polyols</td>
<td>≥ 70 °C</td>
<td>Slow</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aldehydes, sugars</td>
<td>&lt; 50 °C</td>
<td>Moderate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrazine, H&lt;sub&gt;3&lt;/sub&gt;PO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Ambient</td>
<td>Fast</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NaBH&lt;sub&gt;4&lt;/sub&gt;, boranes</td>
<td>Ambient</td>
<td>Very fast</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Citrate</td>
<td>&gt; 70 °C</td>
<td>Moderate</td>
</tr>
<tr>
<td>Ag&lt;sup&gt;+&lt;/sup&gt;</td>
<td>≤ 0.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polyols</td>
<td>&gt;120 °C</td>
<td>Slow</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>70-100 °C</td>
<td>Slow</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&lt; 70 °C</td>
<td>Moderate</td>
</tr>
<tr>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>&lt; 0.7 and ≥ 0</td>
<td>Polyols</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Aldehydes, sugars</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Hydrazine, hydrogen</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>NaBH&lt;sub&gt;4&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.4.2 Synthesis of Gold Nanoparticles

Synthesis of gold nanoparticles by reducing agents such as sodium borohydride [34], ascorbic acid in presence of cetyltrimethylammonium bromide (CTAB) [35], sugars (glucose, fructose and sucrose) [24] have been reported. One common method to synthesize gold nanoparticles is reduction of hydrochloroauric acid, HAuCl<sub>4</sub><sup>-</sup> with sodium citrate, C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>Na<sub>3</sub>. Spherical gold NPs are surrounded by a layer of AuCl<sub>2</sub><sup>-</sup> ions providing a negative charge to the NPs preventing aggregation by electrostatic repulsion [3].
2.4.3 Synthesis of Silver Nanoparticles

Many chemical reduction methods have been used to synthesize silver nanoparticles from silver salts [36-45]. The reactions described here use silver nitrate as the starting material. Chemical reduction methods that have been used to synthesize silver NPs from silver nitrate vary in the choice of reducing agent, the relative quantities and concentrations of reagents, temperature, mixing rate, and duration of reaction. The diameters of the resulting particles depend upon the conditions. Greenish-yellow ($\lambda_{\text{max}}$ 420 nm) colloidal silver with particle sizes from 40 - 60 nm has been reported from reduction with sodium citrate at boiling [46]. Silver colloids described as brownish or yellow-green, with absorption maxima at 400 nm and particle size of about 10 nm, result from reduction with ice-cold sodium borohydride followed by boiling for one hour [47]. A method using both sodium citrate and sodium borohydride at boiling gives a greenish colloid absorbing at 438 nm with particle size 60 - 80 nm [48]. Clear yellow or greenish-yellow colloidal silver can be obtained depending upon the duration of the reaction with ice cold sodium borohydride [49].

2.4.4 Synthesis of Copper Nanoparticles

In contrast with noble metals, such as silver and gold, the synthesis of copper nanoparticles is much more challenging, since copper nanoparticles are fairly unstable in aqueous solution. However, copper costs significantly less than silver and gold, therefore, it is economically attractive. When copper nanoparticles are exposed to air, surface oxidation occurs and ultimately
aggregation appears in a short time. To avoid oxidation, the reduction methods are usually performed under an inert atmosphere (argon, nitrogen) [50, 51], in organic solvents [52, 53] or microemulsion systems [15, 54, 55], and in presence of protective polymers [56-59] or surfactants [13, 18, 60, 61].

In the chemical reduction technique a copper salt is reduced by a reducing agent such as sodium borohydride [14, 50, 61-64], hydrazine (N₂H₄) [25, 57, 65], ascorbate [66], polyol [67], isopropyl alcohol with cetyltrimethylammonium bromide (CTAB) [68], as well as glucose [51]. In the following sections some of the methods to prepare copper nanoparticles are described.

2.4.4.1 Reduction with Sodium Borohydride

Copper nanoparticles were produced by the sodium borohydride reduction of copper ions in aqueous solution and under N₂ atmosphere. The copper sol was yellow with plasmon absorbance at 520 nm. TEM study shows that sizes of particles produced were 4-6 nm [50]. Clear red bright colloidal copper with particle sizes of 8-10 nm (λₘₐₓ 560-565 nm) has been reported from reduction with sodium borohydride in aqueous solution at room temperature. The copper nanoparticles were stabilized by inorganic anions. The reactions were also performed under de-aerated conditions [62]. Reduction of copper bromide (CuBr₂) by sodium borohydride in aqueous solution at room temperature and under inert atmosphere was reported. The mixture yielded a black suspension
following color changes from green-brown to light brown. The particles sizes were 45 nm [63].

### 2.4.4.2 Reduction with Isopropyl Alcohol-CTAB

A method using isopropyl alcohol (IPA) and CTAB gives a violet colloid absorbing at 560 nm with particle size 2-10 nm. CTAB presumably was used as a catalyst for the reduction of copper ions with IPA and as stabilizer to protect copper nanoparticles from oxidation [68].

### 2.4.4.3 Reduction with Glucose

Yellow colloidal copper has been reported from reduction with glucose in alkaline medium and at 80 °C. In this synthesis glucose not only act as a reducing agent and but also stabilizes the copper nanoparticles. Copper nanoparticles synthesized at the two molar ratios of glucose:Cu\(^{2+}\), 22:1 and 44:1, show particles of sizes 20 nm and 4 nm, respectively. The absorption maxima appeared at 499 nm for 22:1 molar ratio and at 463 nm for 44:1 molar ratio. The color in both cases is yellow [51].

### 2.5 Mechanism of Particle Formation

Metal atoms produced by reduction in solutions are essentially insoluble, leading to clusters called embryos through slow aggregation:

\[
xMe^0 \leftrightarrow (Me^0)^n_{em} \quad (2.6)
\]
The existence of very small metal clusters containing a number of atoms correspond to the “magic numbers”, are more stable. The intermediate-sized embryos either dissociate or grow to become stable. Introduction of new metal atoms into the system enable the embryos to reach a critical size and separate from the solution as solid particles, called the nuclei \( \left( Me^0_{n,\text{nucl}} \right) \)

\[
\left( M_{e_x}^0 \right)_{\text{rem}} + y Me^0 \rightarrow \left( Me^0_{x+y,\text{nucl}} \right)
\]  

(2.7)

The nuclei grow to primary nanosize particles through further addition of metal atoms:

\[
\left( Me^0_{n,\text{nucl}} \right) + m Me^0 \rightarrow \left( Me^0_{n+m,\text{pp}} \right)
\]  

(2.8)

At this stage, either the diffusion of atoms onto primary particles continue (diffusion mechanism, eqn 2.9) or nanosize primary particles aggregate to form the final metal particles (aggregation mechanism, eqn 2.10).

\[
\left( Me^0_{\text{pp}} \right) + n Me^0 \rightarrow \left( Me^0_{\text{p}} \right)
\]  

(2.9)

\[
m \left( Me^0_{\text{pp}} \right) \rightarrow \left( Me^0_{\text{p}} \right)
\]  

(2.10)

It is most likely for both growth and aggregation mechanisms to happen simultaneously in the same system. The density and the shape of the final particles depend on which mechanism prevails in the system [33]. Growth mechanism will favor the formation of high density regular shaped metal crystals. Figure 2.7a demonstrates copper nanocubes by this mechanism. Metal particles
produced via aggregation will be mostly spherical and with a lower density.

Figure 2.7b displays gold particles produced by this mechanism.

![Figure 2.7](image)

**Figure 2.7.** (a) SEM images of Cu nanocubes synthesized with ascorbic acid as a reducing agent and PVP as a capping agent [66]. (b) SEM of gold particles obtained by reduction of HAuCl₄ with ascorbic acid [33].

The final size depends on the supersaturation, the fraction of metal atoms involved in the nucleation step relative to the total amount of metal in the system, and on the degree of aggregation [33]. High supersaturation of metal atoms will generate a large number of nuclei and consume a major fraction of the metals in the system. In this situation if the aggregation mechanism is prevented, further increase in size will occur by incorporation of the remaining metallic species in solution and the final particles will remain in the nanosize range.

In order to produce larger particles (in submicrometer and micrometer range), a small number of the nuclei should be created, consuming only a small fraction of the metal atoms, which next grow by integration of the remaining...
metal in solution. This condition can be achieved by slow reactions, slow addition of metal species into system [65, 66] or added seeds [50, 58].

2.6 Applications of Silver and Gold Nanoparticles

Compared with organic dyes the absorption of light by gold and silver nanoparticles is 5–6 orders in magnitude higher. This implies that a metal NP is over 1 million fold more likely than the comparable dye to absorb light, such as near-Infrared (NIR) light and convert it into thermal energy. As a result, these nanoparticles have recently been used in thermal therapy and optical imaging of tumors [69, 70].

Silver and gold nanostructures have been studied as important colorimetric sensors due to their high extinction coefficient. The sensitivity of surface plasmon peaks to environmental changes can lead to optical detection of binding materials on the silver surface. The sensitivity of such an optical sensor is strongly dependent on the size, shape, structure of the nanoparticles, and the surrounding medium. For example, when the refractive index of the surrounding medium changes, the intensity and position of the surface plasmon peak changes. An increase in the refractive index often causes the surface plasmon peak to shift to the longer wavelength. The red shift of the surface plasmon peak can also be caused by the aggregation of the particles and has been used for detection of glucose and protein [70-73]. One example is use of boronic acid-capped silver NPs for detection and monitoring of blood sugar. The interactions of boronic
acid-capped silver NPs and glucose resulted in aggregation of the nanoparticles and were accompanied by an shift in the plasmon peak of silver NPs from 397 nm to 640 nm [74].

The ability of gold and silver nanostructures to enhance local electric fields has led to their applications as surface enhanced Raman scattering (SERS). The enhancement factor can be as much as $10^{14}$-$10^{15}$, which enables the detection of individual molecules absorbed on metal particles [36, 39, 73]. The maximum signal amplification in SER spectroscopy ($10^{15}$) can be achieved with silver particles of about 50 nm [39].

Silver has been known for antibacterial activity since the ancient Greece times. Currently, the investigation of this phenomenon has gained more attention due to the increase of bacterial resistance to antibiotics, caused by their overuse. Silver nanoparticles can be used in medicine to reduce infections in burn treatment, to prevent bacteria colonization on dental materials, stainless steel materials, to eliminate microorganisms on textile fabrics, or they can be used for water treatment [40, 75, 76]. Antimicrobial activity of colloid silver particles is influenced by the dimensions of the particles. The extremely small size of nanoparticles results in the particles having a large surface area relative to their volume. This allows them to easily interact with other particles and increases their antibacterial efficiency.
In heterogeneous catalysis, it is well known that the increasing proportion of surface atoms with decreasing particle size makes small metal particles highly reactive. Silver has been utilized as an oxidation catalyst especially for production of ethylene oxide from ethylene [77].

2.7 Applications of Copper Nanoparticles

Copper nanoparticles, due to their unique physical and chemical properties and low cost preparation, have been of great interest recently. Copper nanoparticles have great applications as heat transfer systems [78], antimicrobial materials [79, 80], super strong materials [81, 82], sensors [83-85], and catalysts [86-88]. Copper nanoparticles can easily oxidize to form copper oxide. If the application requires the copper nanoparticles to be protected from oxidation, the copper NPs are usually encapsulated in organic or inorganic material such as carbon, silica [80, 85, 89, 90]. Some of the copper nanoparticles applications are discussed below.

Copper nanoparticles due to their high surface to volume ratio are very reactive, can easily interact with other particles and increase their antimicrobial efficiency. Colloidal copper has been used as an antimicrobial agent for decades. Copper monodispersed nanoparticles (2-5 nm) imbedded into a polyosilicate called sepiolite (Mg$_8$Si$_{12}$O$_{30}$(OH)$_4$(H$_2$O)$_{4.8}$H$_2$O) have revealed a strong antibacterial activity and were able to decrease the microorganism concentration by 99.9% [79]. Copper nanoparticles (about 6 nm) embedded in polyvinyl
methylketone films exhibit a noticeable inhibitory effect on the growth of microorganisms (E.coli and S. cerevisiae) [80]. Due to the stability of copper nanoparticles supported on a matrix, and their disinfecting properties, copper NPs can be used in paint or plaster as a bactericide agent to coat hospital equipment.

Metallic nanoparticles can be used in heat transfer systems to improve efficiency. Conventional heat transfer fluids have poor heat transfer properties. Fluids containing metallic nanoparticles with a thermal conductivity of about three times that of a pure fluid could double the fluid’s heat transfer rate. It is reported that adding only 0.3 volume percent of copper nanoparticles, with average diameter of less than 10 nm, to ethylene glycol increased its thermal conductivity up to 40% [78].

A major problem facing fuel-cell technologies is formation of high levels of carbon monoxide (CO) which is produced during hydrogen production. One way to eliminate the CO byproduct is to combine it with water to produce hydrogen gas and carbon dioxide (CO₂) in a process known as the “water gas shift” reaction (See reaction below).

\[
CO + H_2O \rightarrow H_2 + CO_2
\]

With the assistance of proper catalysts, the water-shift reaction can convert a large portion of carbon monoxide into carbon dioxide. For this purpose, nanoparticles of either gold or copper supported on a metal oxide (zinc oxide, ZnO and cerium oxide, CeO₂) have been used. In particular, it was found that the
greatest catalytic activity is achieved with extremely small copper or gold
nanoparticles less than 4 nm (2-4 nm) supported on the metal cerium oxide.
Although, gold nanoparticles show the greatest catalytic activity in water-gas shift
reaction, copper is almost as reactive, and its cost is much lower [88].
References


Chapter 3: Synthesis of Silver and Gold Nanoparticles

3.1 Objective

The focus of this project is the synthesis and study of colloidal silver and development of materials for introducing nanotechnology into the chemistry curriculum for university and secondary schools. Nanotechnology laboratory experiments introduce students to unique properties of nanomaterials. For example, the intense yellow color exhibited by silver nanoparticles is compared to ionic or bulk silver. In addition, various sizes of gold nanoparticles are synthesized and correlated with their spectra.

In designing an experiment involving the synthesis of noble metal nanoparticles for a multi-section general chemistry class, cost was an important consideration. Since the hydrogen tetrachloroaurate(III) trihydrate, HAuCl₄·3H₂O used to prepare colloidal gold is more expensive than silver nitrate; the experiment chosen for development was the synthesis and study of colloidal silver. A 25 g quantity of hydrogen tetrachloroaurate(III) trihydrate (0.063 mol) costs $650 compared to $27 for the same mass of silver nitrate (0.15 mol). Per mole, the gold salt is more than 50 times more expensive.

3.2 Experimental

The materials and instruments used to synthesize and characterize silver and gold nanoparticles are presented in this section. Each method for the
synthesis of gold and silver nanoparticles is given in a separate section (3.3.1, 3.4.1).

### 3.2.1 Materials

The silver nitrate (>99% AgNO$_3$), sodium borohydride (99.995% NaBH$_4$), polyvinylpyrrolidone (PVP) with a weight-average number of 10,000 and hydrochloroauric acid (99.99%, HAuCl$_4$) were purchased from Aldrich Chemical Company. Sodium citrate tribasic dehydrate (99% C$_6$H$_5$Na$_3$O$_7$·2H$_2$O) was purchased from Sigma-Aldrich. Distilled water was used. Glassware was cleaned by soaking in alcoholic KOH bath (1 L 95% ethanol + 120 mL water + 120 g KOH). The possibility of aggregation increases if the glassware is not thoroughly clean. All chemicals were used as received without further purification.

### 3.2.2 Instrumentation

Silver and gold nanoparticles were characterized using TEM and UV-Visible spectroscopy. TEM images of silver and gold nanoparticles were obtained on a JEOL 2010 operated at an accelerating voltage of 200KV. Samples were prepared by drying a small drop of the colloidal sol on a carbon-coated 200-mesh copper grid. UV-Visible spectra of the silver and gold colloid sols were obtained using a Perkin Elmer lambda 35 UV-VIS spectrometer.
3.2 Synthesis of Gold Nanoparticles

Colloidal gold is produced by reduction with sodium citrate, C₆H₅O₇Na₃, starting with the gold compound, hydrochloroauric acid, HAuCl₄ [1]. Gold nanoparticles are surrounded by a layer of AuCl₂⁻ ions providing a negative charge to the NPs preventing aggregation by electrostatic repulsion. Larger gold NPs can be produced as the volume of citrate is reduced [1]. TEM was used to find the gold particle sizes prepared with various volumes of citrate (Table 3.1). Plasmon absorbance of gold nanoparticles sols prepared with various volumes of citrate was obtained and results were presented in Table 3.1.

3.3.1 Protocol

Reactions are done in clean dry 125-mL Erlenmeyer flasks (soaked in alcoholic KOH bath and washed with distilled water). A 50 mL gold solution (0.010% w/v) was added to the Erlenmeyer flask and the solution was boiled. Sodium citrate solution 1.0% w/v (1.75 mL) was added to the gold solution all at once with vigorous stirring. The color turned from yellow to blue to red within a few minutes. Boiling and stirring were continued for 10-15 min after the red color appeared. Heat was removed and the mixture was stirred for another 15 min. The mixture was cooled; the volume of the solution should be adjusted by adding distilled water as needed. The solution was stored in a clean brown bottle or covered with foil.
The experiment was repeated with smaller volumes of citrate (1.0, 0.75, 0.5, and 0.3 mL), keeping the volume of gold constant (50 mL). Color of colloidal gold was changed from red (Figure 3.1a) to violet (Figure 3.1b) as the citrate volumes were reduced from 1.75 mL to 0.3 mL. Increasing the volume of citrate (≥ 2 mL) did not produce smaller particles [1].

Figure 3.1. a) Red gold sol prepared with 1.75 ml citrate, b) violet gold sol prepared with 0.3 mL citrate.
3.3.2 Results, Discussion and Characterization of the Gold Nanoparticles

Various particle sizes are obtained upon changing the volume of citrate. Larger gold particles can be produced as the volume of citrate is reduced, for example, 41 nm particles are produced using 0.5 mL citrate compared to formation of 12 nm particles using 1.75 mL citrate (Table 3.1). Transmission electron microscopy was used to find the sizes of gold nanoparticles prepared with various volumes of citrate. Each TEM sample was prepared by drying a small drop of gold nanoparticles from the freshly synthesized sol on a carbon coated 200 mesh copper grid. TEM results for two of the samples (41 nm and 24 nm) are shown in Figure 3.2.

Table 3.1. Relationship between size of gold nanoparticles and volume of sodium citrate.

<table>
<thead>
<tr>
<th>Size nm</th>
<th>1% w/v citrate mL</th>
<th>$\lambda_{\text{max}}$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>1.75</td>
<td>523</td>
</tr>
<tr>
<td>16</td>
<td>1.0</td>
<td>523</td>
</tr>
<tr>
<td>24.5</td>
<td>0.75</td>
<td>526</td>
</tr>
<tr>
<td>41</td>
<td>0.50</td>
<td>550</td>
</tr>
<tr>
<td>71.5</td>
<td>0.30</td>
<td>556</td>
</tr>
</tbody>
</table>
Plasmon absorbance of gold nanoparticles sols prepared with various volumes of citrate was obtained and results are presented in Table 3.1. With increasing particle diameter, the $\lambda_{\text{max}}$ shifts to a longer wavelength. The color of colloidal gold changes from red to violet as the volume of citrate decreases from 1.75 mL to 0.3 mL (Figure 3.1). The UV-Visible spectrum of the red colloidal gold ($\lambda_{\text{max}} = 523$ nm) prepared with 1.75 mL citrate is shown in Figure 3.3.

![Figure 3.2](image)

(a) TEM results for two of the gold samples, a) 24 nm and b) 41 nm. Size bars are 100 nm for both images.
Figure 3.3. UV–VIS absorption spectrum of red colloidal Au ($\lambda_{\text{max}} = 523$ nm) prepared by 1.75 mL citrate 1.0% w/v. To adjust the absorption maximum between 0.5 and 0.7, the product sol was diluted with distilled water.
3.4 Synthesis of Silver Nanoparticles

Yellow colloidal silver has been reported upon reaction with ice-cold sodium borohydride [2] and is the basis for the method used in this work described next.

The determination of an optimal set of conditions for the synthesis of silver nanoparticles is described in the sections that follow. An excess of sodium borohydride is needed both to reduce the ionic silver and to stabilize the silver nanoparticles that form. The chemical reaction is the sodium borohydride reduction of silver nitrate:

\[ AgNO_3 + NaBH_4 \rightarrow Ag + \frac{1}{2} H_2 + \frac{1}{2} B_2H_6 + NaNO_3 \]

The silver particle sizes are 12 ± 2 nm. The plasmon absorbance is near 400 nm and the peak width at half maximum (PWHM) is 50–70 nm. The relationship between aggregation and optical properties is investigated along with a method to protect the particles using polyvinylpyrrolidone.

Results were used to develop a laboratory experiment on synthesis and study of silver nanoparticles. The experiment was conducted in two general chemistry laboratory classes (24 student pairs). Outcome obtained in these laboratory classes is given along with student reactions to the experiment.
3.4.1 Protocol

Reactions were done in clean dry 125-mL Erlenmeyer flasks. A 10-mL volume of 1.0 mM silver nitrate was added dropwise (about 1 drop/second) to 30 mL of 2.0 mM sodium borohydride solution that had been chilled in an icebath. The reaction mixture was stirred vigorously on a magnetic stir plate. The solution turned light yellow after the addition of 2 mL of silver nitrate and a brighter yellow (Figure 3.4a) when all of the silver nitrate had been added. The entire addition took about three minutes, after which the stirring was stopped and the stir bar removed. The clear yellow colloidal silver shown in Figure 3.4a, is stable at room temperature stored in a transparent vial for as long as several weeks or months. Upon aggregation the colloidal silver solution turns darker yellow (Figure 3.4b), violet (Figure 3.4c), and then grayish (Figure 3.4d).

![Figure 3.4](image)

**Figure 3.4.** Colloidal silver in various stages of aggregation, a) clear yellow sol, b) dark yellow, c) violet, and d) grayish, as aggregation proceeds.
3.4.2 Results and Discussion

Reaction conditions, including stirring time and relative quantities of reagents (both the absolute number of moles of each reactant as well as their relative molarities), must be carefully controlled to obtain stable yellow colloidal silver. If stirring is continued once all of the silver nitrate has been added, aggregation begins as the yellow sol first turns a darker yellow (Figure 3.4b), then violet (Figure 3.4c), and eventually grayish (Figure 3.4d), after which the colloid breaks down and particles settle out. Similar aggregation may also occur if the reaction is interrupted before all of the silver salt has been added. It was also found that the initial concentration of sodium borohydride must be twice that of silver nitrate: \([\text{NaBH}_4]/[\text{AgNO}_3] = 2.0\). When concentration of borohydride was varied from 2.0 mM while using 1.0 mM silver nitrate, breakdown of the product took place in less than an hour (Table 3.2).

**Table 3.2.** Effect on the stability of Ag nanoparticles when concentration of NaBH\(_4\) is varied. Concentration of AgNO\(_3\) is constant at 1.0 mM.

<table>
<thead>
<tr>
<th>([\text{NaBH}_4]/[\text{AgNO}_3])</th>
<th>(^a\text{Stability time, min})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>Stable</td>
</tr>
<tr>
<td>2.1</td>
<td>(~30)</td>
</tr>
<tr>
<td>1.9</td>
<td>(~20)</td>
</tr>
<tr>
<td>1.8</td>
<td>(~5)</td>
</tr>
</tbody>
</table>

\(^a\text{Stability time is the time when solution turns yellow to when it turns gray (onset of aggregation).}\)
Occasionally the purity of “99% sodium borohydride” could be lower for a particular batch #. Using a newly purchased bottle of sodium borohydride, we found that every attempt to repeat the synthesis failed and resulted in aggregated product. When we contacted Aldrich, we were informed that the purity of that particular batch was only 98.39, compared to all other batches that we used, which were 98.9%. Instead, somewhat more expensive 99.995% sodium borohydride can be used.

3.4.3 Characterization of Silver Nanoparticles

Silver nanoparticles were examined using UV-VIS spectroscopy and TEM.

3.4.3.1 Optical Characterization

The distinctive colors of colloidal gold and silver are due to a phenomenon known as plasmon absorbance. Incident light creates oscillations in conduction electrons on the surface of the nanoparticles and electromagnetic radiation is absorbed (See Section 2.3). The spectrum of the clear yellow colloidal silver from the synthesis above (Section 3.4.1) is shown in Figure 3.5. The plasmon resonance produces a peak near 400 nm, with PWHM of 50 to 70 nm. The wavelength of the plasmon absorption maximum in a given solvent can be used to indicate particle size [50] (See section 3.4.3.2).
Figure 3.5. UV–VIS absorption spectrum of clear yellow colloidal Ag ($\lambda_{\text{max}} = 400$ nm). To adjust the absorption maximum between 0.5 and 0.7, the product sol was diluted with distilled water.

3.4.3.2 Particle Size Measurement Using TEM

Silver nanoparticles that produced the spectrum in Figure 3.5 were examined using transmission electron microscopy. A sample of silver nanoparticles from a freshly synthesized clear yellow sol was prepared by drying a small drop on a carbon-coated 200-mesh copper grid. The TEM image of one region of the sample is shown in Figure 3.6, and the size distribution is shown in Figure 3.7. The TEM image shows the silver particles are spherical with sizes of $12 \pm 2$ nm.

In general, as the particles become larger the absorption maximum shifts to longer wavelengths and the peaks broaden. The peak width at half the
absorption maximum is PWHM. Values for silver particle size, plasmon maxima, and PWHM that have been reported are listed in Table 3.3.

**Table 3.3.** Particle size and spectral features of silver nanoparticles.

<table>
<thead>
<tr>
<th>Particle size nm</th>
<th>$\lambda_{\text{max}}$ nm</th>
<th>PWHM Nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>10–14$^a$</td>
<td>395–405</td>
<td>50-70</td>
</tr>
<tr>
<td>35–50$^b$</td>
<td>420</td>
<td>100–110</td>
</tr>
<tr>
<td>60–80$^c$</td>
<td>438</td>
<td>140–150</td>
</tr>
</tbody>
</table>

$^a$Data from this work, reference 3. $^b$Data from reference 4. $^c$Data from reference 5.

**Figure 3.6.** TEM images of silver nanoparticles (12 ± 2 nm).
3.4.4 Stability of Colloidal Silver

Stability of silver NPs was investigated by measuring the absorption spectra of the silver colloidal sol of the same sample prepared by the method in section 3.4.1 at various times. The sample was stored at room temperature in a transparent vial and UV-Visible spectra of the sample were taken after the formation of yellow silver colloid sol (plasmon absorbance at 397 nm) then after one week, two weeks, one month, and two months. The results indicate that there is no obvious difference in position and symmetry of absorption peak during the initial two weeks (Figure 3.8). After four weeks, the position of the peak has a slight red shift (from 397 to 402 nm), suggesting the formation of larger particles without any aggregation. Even after two months the plasmon absorbance remained at 404 nm and no aggregation was observed. Thus, colloidal silver can remain stable at room temperature for as long as several weeks or months. The reason for the stability of the colloid silver sol is described in the next section.

Figure 3.7. TEM-derived Ag nanoparticle size distribution.
3.4.5 Aggregation

The possibility of aggregation during the synthesis was discussed in Section 3.4.1. Adsorption of borohydride plays a key role in stabilizing growing silver nanoparticles by providing a particle surface charge as shown in the schematic diagram in Figure 3.9. There must be enough borohydride to stabilize the particles as the reaction proceeds. However, later in the reaction too much sodium borohydride increases the overall ionic strength and aggregation will occur. The aggregation can also be brought about by addition of electrolytes such as NaCl. Nanoparticles are kept in suspension by repulsive electrostatic forces between the particles owing to adsorbed borohydride (Figure 3.9). Salt shields the charges allowing the particles to clump together to form aggregates [6-9]. The colloidal silver solution turns darker yellow, violet, and then grayish (See Figure 3.4). The visible spectrum of the violet solution pictured in Figure 3.4 is shown in

Figure 3.8: UV-VIS spectra of colloidal silver nanoparticles stored for different lengths of time.
Figure 3.10. A new broad peak around 525 nm appears along with a decrease in the intensity of the plasmon absorbance which indicates onset of aggregation.

Nanoparticles in colloidal sols can also be stabilized by adsorbed polyvinylpyrrolidone (PVP) [10-14]. The structures of the monomer, vinylpyrrolidone, and the repeat unit of PVP are shown in Figure 3.11. The concentration of PVP needed to prevent aggregation can be found by adding one drop of aqueous PVP to a 5-mL volume of yellow silver sol, then testing for stabilization by adding 1–2 drops of 1.5 M NaCl. Using 0.3% PVP the sol remains yellow and stable. The procedure is repeated with diluted PVP until aggregation is observed upon addition of salt. The minimum concentration of PVP required to stabilize the sol synthesized according to the method described here was 0.01%.

Figure 3.9. Repulsive forces separate Ag nanoparticles (NP) with adsorbed borohydride.
Figure 3.10. UV–VIS absorption spectrum of violet sol.

Figure 3.11. The structures of the monomer, vinylpyrrolidone (left), and the repeat unit of PVP (right).
3.4.6 Student Results and Evaluation

The work described in Sections 3.4.1 through 3.4.5 resulted in designing an experiment on synthesis of silver nanoparticles that was published in Journal of Chemical Education, February 2007 issue [3]. The experiment has also been made available nationwide through the Interdisciplinary Education Group on a website established at University of Wisconsin – Madison [15].

A formative evaluation was conducted during the general chemistry lab in the spring 2006 quarter at Drexel University. This experiment was performed by 24 pairs of general chemistry students. To modify the procedure, students’ lab data, and their performances in lab were studied, corrections were made prior to the next lab. Lab instructors were also asked to provide comments, and discuss any problems encountered by students. The new procedure was evaluated again during the following lab session and the results were used to revise the procedure. The final lab documentation is found in Appendix A.

Students described the appearance of their product as “yellow” or “golden” and found a value for $\lambda_{\text{max}}$ (using a Spectronic-20) near 400 nm. In one instance, aggregation took place and the product was described as “black with gray particles”. Students were asked to write comments about the experiment. They enjoyed the experiment and were particularly impressed by the color of the silver nanoparticles. “I thought the experiment was very interesting”, said one student, “because I never knew that elements could have different properties when
their size is changed”. And from others, “I found it interesting that properties of matter can change on a nanolevel” and “it was certainly intriguing to see the color change from silver to yellow. This was definitely a worthwhile experiment.”

3.5 Conclusion

Colloidal silver nanoparticles were synthesized by borohydride reduction of silver nitrate. UV – VIS spectrum confirms the appearance of plasmon absorbance near 400 nm, and TEM images show that the particle sizes are about 12 nm. The yellow colloidal silver remains stable for as long as several weeks or months. The possibility of aggregation was investigated caused by addition of electrolytes, such as NaCl. Silver nanoparticles in colloidal sols can be stabilized by adsorbed PVP. The minimum concentration of PVP required to stabilize the sol prepared was found to be 0.01%. Results were used to develop a laboratory experiment on synthesis and study of silver nanoparticles (Appendix A), which has also been made available nationwide through the Interdisciplinary Education Group on a website established at University of Wisconsin – Madison. The lab experiment to produce silver nanoparticles is easy, convenient, can be done on the bench top, and requires simple equipment.

Colloidal gold was synthesized by citrate reduction of hydrochloroauric acid, HAuCl₄. Larger gold particles were produced as the volume of citrate was reduced. Particle sizes from 12 nm to 71.5 nm were formed when volume of citrate was reduced from 1.75 mL to 0.3 mL. The plasmon absorbance increases
from 523 nm to 556 nm as volume of citrate is reduced from 1.75 mL to 0.3 mL.

When larger volume of citrate is used (≥2 mL), no reduction in particle size is observed.
References


Chapter 4: Synthesis of Copper Nanoparticles

4.1 Objective

The focus of this project is two fold. The primary goal is to improve the synthesis of copper nanoparticles (NPs). The secondary purpose is to create materials for introducing nanotechnology into the chemistry curriculum for university and secondary schools (See Section 3.1).

The synthesis of copper nanoparticles costs less than both silver and gold NPs. In addition, readily available and inexpensive household chemicals such as root killer ($\text{CuSO}_4\cdot5\text{H}_2\text{O}$), lye ($\text{NaOH}$) and glucose tablets can be used to synthesize copper NPs. However, copper nanoparticles are easily oxidized making the synthesis of stable colloidal copper relatively difficult compared to colloidal silver and gold.

4.2 Introduction

Four methods were used for the synthesis of copper nanoparticles. Copper nanoparticles were prepared by reduction of copper(II) sulfate in aqueous solution with: (i) borohydride, (ii) borohydride and potassium iodide as protecting agent, (iii) reducing sugars, and (iv) reduction of copper nitrate in isopropanol (IPA) in presence of cetyltrimethylammonium bormide (CTAB). These methods are easy, convenient and can be done on the bench top. The stability of copper
nanoparticles is an issue. Thus, the attempt was made to find a method which produces more stable colloidal copper.

The reactions listed above for the synthesis of colloidal copper can be done in the presence of air by reduction of copper(II) salts:

\[ mCu^{2+} + 2Red \rightarrow mCu^0 + 2Ox \]

The production of copper nanoparticles is followed by the appearance of a color, due to the typical surface plasmon resonance which has a maximum near 560 nm. Particle size was determined using both atomic force microscopy and transmission electron microscopy.

Sections below include details of four different synthetic methods that produce copper nanoparticles, all of which can be performed in a flask open to the air. The products are stable for periods of time ranging from a few minutes to a week (this is in contrast to colloidal silver and gold that can remain stable for months). For each reaction, the effect of some parameters such as reagent concentrations, relative amounts of reducing agent and copper salt, temperature and additives on stability of the copper nanoparticles (NPs) were investigated.

A procedure for making colloidal copper from household materials will be described in Section 4.7.5.
4.3. Experimental

The materials and instruments for all four methods used to synthesize and characterize copper nanoparticles are presented in this section. Each method for the synthesis of copper nanoparticles is given in a separate section (Sections 4.4 to 4.7).

4.3.1 Materials

Copper(II) sulfate pentahydrate (99.995% CuSO₄·5H₂O) and copper(II) chloride dihydrate (99.999% CuCl₂·2H₂O) were purchased from Sigma-Aldrich Chemical Company. Copper(II) nitrate hemipentahydrate (99.99% and 98% Cu(NO₃)₂·2.5H₂O), copper(II) nitrate hydrate (99.999% Cu(NO₃)₂·H₂O), sodium borohydride (99.995% NaBH₄), poly(vinylpyrrolidone) (PVP) with a weight-average number of 10,000 and cetyltrimethylammonium bormide (CTAB) were purchased from Aldrich Chemical Company. Potassium iodide (KI), sodium hydroxide (NaOH), glucose, fructose, lactose and citric acid anhydrous were purchased from Fisher Scientific Company. Isopropyl alcohol (99% IPA) was purchased from Pharmco-AAPER Company. Technical Copper(II) sulfate pentahydrate (CuSO₄·5H₂O) was purchased from Flinn Scientific Inc. Root Killer (CuSO₄·5H₂O), lye (NaOH), three different brands of glucose tablets (B.D, Dex, Rite Aid) and vitamin C (ascorbic acid) were purchased from hardware or convenience stores. All chemicals were used as received without further purification.
Distilled water was used. Glassware was cleaned by soaking in alcoholic KOH bath (1 L 95% ethanol + 120 mL water + 120 g KOH). The possibility of aggregation increases if the glassware is not thoroughly clean.

The influence of copper(II) salt purity on the synthesis of copper NPs is discussed in the following section.

4.3.2 Copper(II) Salt Purity

The effect of purity of the Cu(II) salt was investigated for two synthesis methods, sodium borohydride reduction (Section 4.4) and alcohol reduction/CTAB (Section 4.6), and results are summarized in Tables 4.1 and 4.2.

Equal volumes of 0.0010 M copper(II) and 0.020 M sodium borohydride were mixed for all the samples in Table 4.1. For the borohydride reduction method the production of nanoparticles is followed by color change to red and the appearance of the plasmon absorbance near 560 nm. Aggregation is observed by color change from red to dark blue (blue-black) and disappearance of plasmon absorbance (See Section 4.4.2).
Table 4.1. The effect of purity of Cu(II) salt on the stability of copper nanoparticles in sodium borohydride reduction method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu(II) salt</th>
<th>( \lambda_{\text{max}}, \text{nm} )</th>
<th>Color</th>
<th>(^*)Stability time min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu(NO_3)_2·H_2O</td>
<td>560</td>
<td>Red</td>
<td>360</td>
</tr>
<tr>
<td>2</td>
<td>CuSO_4·5H_2O</td>
<td>560</td>
<td>Red</td>
<td>360</td>
</tr>
<tr>
<td>3</td>
<td>CuSO_4·5H_2O</td>
<td>560</td>
<td>Red</td>
<td>300</td>
</tr>
<tr>
<td>4</td>
<td>Root Killer, CuSO_4·5H_2O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Technical, CuSO_4·5H_2O</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^*\)The stability time is the time when solution turns red to when it turns dark blue (onset of aggregation).

Equal volumes of isopropyl solutions of 0.0030 M copper(II) nitrate and 0.090 M CTAB were mixed for all the samples in Table 4.2. In alcohol reduction/CTAB method the color change to violet indicates production of nanoparticles. All the copper sols in Table 4.2 were stable for one week (See section 4.7.2).

Table 4.2. The effect of purity of Cu(NO_3)_2 salt on copper nanoparticles stability in isopropyl/CTAB reduction method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu(II) salt</th>
<th>( \lambda_{\text{max}}, \text{nm} )</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu(NO_3)_2·H_2O</td>
<td>556±3</td>
<td>Dark violet</td>
</tr>
<tr>
<td>2</td>
<td>Cu(NO_3)_2·2.5H_2O</td>
<td>563±3</td>
<td>Dark violet</td>
</tr>
<tr>
<td>3</td>
<td>Cu(NO_3)_2·2.5H_2O</td>
<td>560±3</td>
<td>Dark violet</td>
</tr>
</tbody>
</table>
No difference in plasmon absorbance and stability of copper nanoparticles was observed when the purity of copper salt was reduced from 99.999% to 99.995% or 99.99% or even as low as 98%. Copper sulfate pentahydrate 99.995% was used for all of the experiments in Sections 4.4, 4.5 and 4.7. Copper(II) nitrate hemipentahydrate 99.99% was used for the experiments performed with IPA/CTAB (Section 4.6).

4.3.3 Instrumentation

Copper nanoparticles were characterized using TEM, AFM and UV-Visible spectroscopy. TEM images of copper nanoparticles were obtained on a JEOL 2010 operated at an accelerating voltage of 200KV. Samples were prepared by drying a small drop of copper colloidal sol on a carbon-coated 200-mesh copper grid. AFM images of copper nanoparticles were performed on a Nanosurf® EasyScan DFM. The AFM tip was made of silicon (Si) with a radius of less than 10 nm. AFM samples were prepared by drying 15-20 µL of copper colloid sol on a 9.9 mm mica disc mounted on a 15 mm AFM disc. UV-Vis spectra of the copper colloid sol were obtained using a Perkin Elmer lambda 35 UV-Vis spectrometer.
4.4 Synthesis of Copper Nanoparticles by Reduction with Sodium Borohydride

The synthesis method by reduction with sodium borohydride, the protocol, results, discussion and characterization of copper nanoparticles with UV-Visible spectroscopy and AFM are presented in this section.

4.4.1 Synthesis Method

One reaction that has been used for the synthesis of copper nanoparticles is the sodium borohydride reduction of a copper salt [1, 2].

\[ Cu^{2+} + 2BH_4^- \rightarrow Cu + H_2 + B_2H_6 \]

The method produces a reddish sol containing 52 nm particles measured by AFM with plasmon absorbance near 560 nm (Figure 4.1).

According to the reaction above, the stoichiometric amount of borohydride is twice the number of moles of copper salt. An excess of sodium borohydride is required both to reduce the copper(II) and to stabilize the nanoparticles that form. The reactions are run by combining dilute aqueous copper sulfate and excess sodium borohydride.
4.4.2 Protocol

Reactions were done in clean dry 125-mL Erlenmeyer flasks (soaked in alcoholic KOH bath and washed with distilled water) open to the air. Volumes were measured using a graduated cylinder. In a typical reaction, dilute copper(II) solution was poured into dilute freshly prepared sodium borohydride solution. The addition was done in several parts over a period of about two minutes while swirling the flask. The mixture turned first yellow, then orange and finally red. The appearance of a reddish color indicated the presence of copper nanoparticles (See Figure 4.2 right). The plasmon absorbance near 560 nm was present in a spectrum taken within minutes after the color appeared (Figure 4.1). The reddish

**Figure 4.1.** UV–VIS absorption spectrum of red colloidal Cu ($\lambda_{\text{max}} = 558$ nm) which was prepared by the method in Section 4.4.2 and with the BH$_4^-$:Cu$^{2+}$ mole ratio of 20:1.
product, stored in a closed vial was stable from two hours up to six hours. However, once the vial is opened, it takes about 5-15 min for aggregation to take place. Upon aggregation, there is a change in color to dark blue followed by formation of particles as shown in Figures 4.2 (middle) and 4.2 (left), respectively.

![Figure 4.2](image)

**Figure 4.2.** Freshly prepared red Cu sol (right), dark blue color (middle) upon onset of aggregation, particles form (left).
4.4.3 Results and Discussion

To determine optimal conditions for synthesis of stable copper NPs via borohydride reduction of copper(II) salts, the following were varied and results are summarized in Tables 4.3-4.6:

- Relative molarities of reactants
- Relative moles of reactants
- Use of additives
- Temperature
- Stirring

The Tables 4.3-4.5 were sorted according to the increasing stability of copper nanoparticles. The stability time is the time when solution turns red to when it turns dark blue (onset of aggregation).

To compare the effect of copper nitrate versus copper sulfate, samples in Table 4.3 were prepared via borohydride reduction of copper sulfate and samples in Table 4.4 were prepared by borohydride reduction of copper(II) nitrate. The use of copper nitrate versus copper sulfate has no effect on the production of stable copper NPs. Also it was found that the order of addition of copper(II) and borohydride solution did not influence the formation of product or stability of copper NPs. Thus, all the samples in Tables 4.3-4.4 were prepared by addition of copper(II) to borohydride solution.
Table 4.3. Addition of 0.0010 M CuSO₄·5H₂O to borohydride under varying conditions. Samples were kept in closed vials at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[BH₄⁻]</th>
<th>mol BH₄⁻</th>
<th>Temp ⁰C</th>
<th>aRxn time, min and color</th>
<th>bStability time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>2.0</td>
<td>RT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>4.0</td>
<td>RT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>6.0</td>
<td>Ice-cooled</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>10</td>
<td>RT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>4.0</td>
<td>Ice-cooled</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>90</td>
<td>RT</td>
<td>120, Orange</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>20</td>
<td>90</td>
<td>Ice-cooled</td>
<td>150, Orange</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>90</td>
<td>RT</td>
<td>120, Orange</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>100</td>
<td>1.0</td>
<td>Ice-cooled</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>4.0</td>
<td>4.0</td>
<td>RT</td>
<td>10, Red 20</td>
<td></td>
</tr>
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<td>11</td>
<td>6.0</td>
<td>6.0</td>
<td>RT</td>
<td>30, Red 30</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>30</td>
<td>6</td>
<td>RT</td>
<td>20, Red 40</td>
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<td>13</td>
<td>20</td>
<td>8.0</td>
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<td>30, Red 90</td>
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<tr>
<td>14</td>
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<td>10</td>
<td>RT</td>
<td>35, Red 120</td>
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</tr>
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<td>15</td>
<td>50</td>
<td>10</td>
<td>RT</td>
<td>20, Red 120</td>
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</tr>
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<td>30, Red 150</td>
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<td>RT</td>
<td>30, Red 150</td>
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<td>40, Red 180</td>
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<tr>
<td>20</td>
<td>15</td>
<td>15</td>
<td>Ice-cooled</td>
<td>60, Red 180</td>
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<td>10</td>
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<td>RT</td>
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<td>20, Red 300</td>
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<td>RT</td>
<td>60, Red 300</td>
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<tr>
<td>28</td>
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<td>36</td>
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<td>90, Red 300</td>
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<td>45</td>
<td>RT</td>
<td>120, Red 300</td>
<td></td>
</tr>
<tr>
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<td>30</td>
<td>60</td>
<td>RT</td>
<td>150, Red 300</td>
<td></td>
</tr>
<tr>
<td>31</td>
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<td>60</td>
<td>Ice-cooled</td>
<td>180, Red 300</td>
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<td>50</td>
<td>20</td>
<td>RT</td>
<td>30, Red 300</td>
<td></td>
</tr>
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<td>33</td>
<td>20</td>
<td>60</td>
<td>RT</td>
<td>150, Red 360</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>20</td>
<td>20</td>
<td>Ice-cooled</td>
<td>90, Red 360</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>20</td>
<td>20</td>
<td>RT</td>
<td>60, Red 360</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>20</td>
<td>40</td>
<td>RT</td>
<td>90, Red 360</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>20</td>
<td>40</td>
<td>Ice-cooled</td>
<td>120, Red 360</td>
<td></td>
</tr>
</tbody>
</table>

aThe reaction time is the time from when the reagents were mixed to when the red color appears.

bThe stability time is the time when solution turns red to when it turns dark blue (onset of aggregation).

a, bThe data is average of three readings, with error of about ±10%.
Table 4.4. Addition of 0.0010 M Cu(NO₃)₂·H₂O to borohydride under varying conditions. Samples were kept in closed vials at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[BH₄⁻] [Cu²⁺]</th>
<th>mol BH₄⁻/ mol Cu²⁺</th>
<th>Temp °C</th>
<th>aRxn time, min and color</th>
<th>bStability time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>1.0</td>
<td>Ice-cooled</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>2.0</td>
<td>Ice-cooled</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>4.0</td>
<td>Ice-cooled</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>6.0</td>
<td>Ice-cooled</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.0</td>
<td>10</td>
<td>Ice-cooled</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>60</td>
<td>RT</td>
<td>150, Red</td>
<td>360</td>
</tr>
<tr>
<td>7</td>
<td>20</td>
<td>20</td>
<td>Ice-cooled</td>
<td>90, Red</td>
<td>360</td>
</tr>
<tr>
<td>8</td>
<td>20</td>
<td>40</td>
<td>RT</td>
<td>90, Red</td>
<td>360</td>
</tr>
</tbody>
</table>

a, bThe data is average of three readings, with error of about ±10%.

4.4.3.1 Relative Molarities of Reactants and Relative Moles of Reactants

The tables above (Table 4.3 and 4.4) are sorted according to increasing stability. The stability time is the time when the solution turns red to when it turns dark blue (onset of aggregation). If no red color appears, there is no plasmon resonance (SPR), no product and of course, stability cannot be recorded. Formation and stability of product depends on the mole ratio (mol BH₄⁻/mol Cu²⁺). There must be enough borohydride to stabilize the particles as the reaction proceeds. No product forms when the ratio of moles is less than 6. In every case in which SPR is observed and stability can be recorded:
However, too much sodium borohydride increases the overall ionic strength, preventing the formation of stable nanoparticles (Samples 6, 7, and 8 in Table 4.3). Longer periods of stability, four to six hours, are observed when the mole ratios are greater than 20 (Samples 20 to 37). Increasing the mole ratio to 60 (Samples 30 and 31) only increases the reaction time but does not increase the stability of copper NPs.

Relative molar concentration ([BH\textsubscript{4}\textsuperscript{-}]/[Cu\textsuperscript{2+}]) is also important. It can be seen that product does not form when concentration ratios are less than 2, even though the mole ratios are $\geq 6$ (Samples 3 and 4 in Table 4.3).

The results when the starting salt is copper nitrate (Table 4.4) are very similar.

4.4.3.2 Stirring Effect

All the samples in Tables 4.3 and 4.4 were prepared according to the procedure in Section 4.4.2, without stirring the mixture. To study the effect of stirring on the stability of copper colloid, two samples with BH\textsubscript{4}\textsuperscript{-}:Cu\textsuperscript{2+} mole ratios of 20:1 and 30:1 were prepared. For each sample the mixture was stirred vigorously with a magnet bar while copper(II) was added to the solution. No change in the reaction time and stability of copper NPs was observed compared to
the procedure typical used when the reaction mixture was gently mixed by swirling the flask.

4.4.3.3 Temperature Effect

The temperature has an important effect on the stability of copper NPs sol and reaction time. Four samples were prepared (according to the procedure in Section 4.4.2 and with BH$_4$⁻:Cu$^{2+}$ mole ratio of 20:1) with the ice-cooled borohydride, room temperature borohydride and borohydrides that had been heated on a hot water bath at 45 °C and 60 °C. Increasing the temperature of the borohydride solution to 60 °C decreases the reaction time and the stability of the copper NPs as shown in the plot in Figure 4.3. The reactions are not thermostatted after mixing.

![Temperature Effect](image)

**Figure 4.3.** Plot of the temperature vs. the reaction time and the stability time. Sample was prepared according to the procedure in Section 4.4.2 with BH$_4$⁻:Cu$^{2+}$ mole ratio of 20:1. The data for the stability time and the reaction time is average of three readings, with error of about ±10%.
At higher temperature the particles grow more rapidly, and aggregation takes place at a higher rate. It is also known that the particle surface charge arises from the adsorption of borohydride which provides repulsive electrostatic forces between the particles and prevents them from clumping together. As the reaction temperature is increased, the rate of borohydride consumption increases, thus causing the particles to be less stable [3].

4.4.3.4 Use of Poly(vinylpyrrolidone), PVP

In the preparation of metal nanoparticles by chemical reduction Poly(vinylpyrrolidone), PVP, has been used as a stabilizer [4-7]. PVP was added to samples prepared by borohydride reduction to observe if it protected the copper nanoparticles from aggregation. Samples were prepared by mixing equal volumes of copper(II) (0.0010 M) and borohydride and according to the procedure in Section 4.4.2. The results are summarized in Table 4.5. The PVP was added after the color turned orange (See Section 4.4.4.1) with two exceptions, that is, when PVP was added immediately after addition of Cu(II) to borohydride (Sample 6) and when Cu(II) was added to the mixture of borohydride and PVP (Sample 7). In all cases, the colors of reactions turned green or brown-red. In the UV-Visible spectrum of one of the brown-red products (Figure 4.4) the absorption band is less intense than the typical plasmon absorbance for red products.
PVP did not protect the copper nanoparticles from aggregation. For example, for Sample 10 the stability time is 300 min. This is similar for the sample with the same mole ratio prepared without PVP (Sample 27 in Table 4.3).

Table 4.5. The effect of PVP on the stability of copper nanoparticles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>([\text{BH}_4^-]/[\text{Cu}^{2+}])</th>
<th>PVP 0.3% mL</th>
<th>aRxn time, min and color</th>
<th>bStability time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.0</td>
<td>2</td>
<td>Green</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6.0</td>
<td>5</td>
<td>Green</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6.0</td>
<td>10</td>
<td>Green</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>2</td>
<td>60, Brown-red</td>
<td>120</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>10</td>
<td>90, Brown-red</td>
<td>180</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>5</td>
<td>Green</td>
<td>180</td>
</tr>
<tr>
<td>7</td>
<td>20</td>
<td>5</td>
<td>90, Brown-red</td>
<td>180</td>
</tr>
<tr>
<td>8</td>
<td>20</td>
<td>2</td>
<td>60, Brown-red</td>
<td>300</td>
</tr>
<tr>
<td>9</td>
<td>20</td>
<td>5</td>
<td>60, Brown-red</td>
<td>300</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>5</td>
<td>60, Brown-red</td>
<td>300</td>
</tr>
</tbody>
</table>

a, b The data is average of three readings, with error of about ±10%.
4.4.4 Characterization of Copper Nanoparticles Prepared via Borohydride Reduction

Copper nanoparticles were characterized using UV-Visible spectroscopy and AFM.

4.4.4.1 Optical Characterization

Upon mixing sodium borohydride and copper(II) solutions the reaction turns first yellow, light orange, then orange, and finally red. Plasmon absorbance (near 560 nm) appears only when the color of solution is red. The spectrum of the clear red colloidal copper (Figure 4.2) from the synthesis above (See Section 4.4.2) is shown in Figure 4.1. The sample was prepared by reduction of 0.0010 M copper sulfate with an equal volume of 0.020 M sodium borohydride at room
temperature. Upon aggregation the color changes from red to dark blue and ultimately black particles appear (Figure 4.2).

The plasmon absorbance cannot be seen for the yellow color reaction mixture and the absorbance is very weak when it turns orange which probably indicates onset of particle formation. Surface plasmon absorbance is very broad for the small particles with diameters below 4 nm. As the particles grow and the number of the particles increases, the surface plasmon absorbance narrows and increases in intensity [8, 9], the color becomes orange and finally red for the sols that absorb near 560 nm. The spectra of the yellow, light orange, orange and red reaction mixture of the same sample are shown in Figure 4.5.

![UV-VIS absorption spectra](image)

**Figure 4.5.** UV-VIS absorption spectra of yellow, light orange, orange and red color ($\lambda_{\text{max}} = 564$ nm) reaction mixture.
4.4.4.2 Particle Size Measurement Using Atomic Force Microscopy

Copper nanoparticles that produced the spectrum in Figure 4.1 \((\lambda_{\text{max}} = 560 \text{ nm})\) were characterized using AFM. A sample was prepared by drying 15-20 µL of a freshly synthesized clear red sol on a 9.9 mm mica disc. The AFM image of one region of the sample is shown in Figure 4.6, and the size distribution is shown in Figure 4.7. The AFM image shows the copper particles are polydisperse with mean sizes of 52 nm.

Figure 4.6. (10.3 µm x 10.3 µm) AFM image of Cu NPs which was prepared by the method in Section 4.4.2 and with the BH₄⁻:Cu²⁺ mole ratio of 20:1.
Figure 4.7. AFM-derived Cu nanoparticle size distribution.
4.5 Synthesis of Copper Nanoparticles by Reduction with Borohydride in Presence of Iodide

The synthesis method by reduction with sodium borohydride in presence of iodide, the protocol, results, discussion and characterization of copper nanoparticles with UV-Visible spectroscopy, AFM and TEM are presented in this section.

4.5.1 Synthesis Method

In the reaction discussed here iodide stabilizes the copper nanoparticles produced by the borohydride reduction of copper sulfate [10]. The method produces a reddish sol with plasmon absorbance near 560 nm and particle sizes of about 20 nm. The reaction of copper(II) and borohydride was illustrated in Section 4.4.1. An excess of sodium borohydride is needed both to reduce the copper(II) and to stabilize the nanoparticles that form. In this method dilute borohydride is added to a solution containing copper(II) and iodide.

4.5.2 Protocol

Reactions were done in clean dry 125-mL Erlenmeyer flasks open to the air. Volumes were measured using a graduated cylinder. In a typical reaction, dilute borohydride solution was added into a dilute solution containing copper(II) sulfate and potassium iodide that had been heated on a hot water bath (35-40 °C) for 10 minutes. The addition was done in several parts over a period of about two minutes while swirling the flask. The reaction mixture turned first yellow, light orange, then orange and finally red in 10 to 20 minutes. The appearance of a
reddish color indicated the presence of copper nanoparticles (Figure 4.8a). The plasmon absorbance near 560 nm was present in a spectrum taken within minutes after the color appeared. The reddish product, stored in a closed vial is stable for a few hours. However, once the vial is opened, it takes about 5-15 min for aggregation to take place. Upon aggregation, the reddish sol first turns yellow (Figure 4.8b), after which yellowish particles form (Figure 4.8c). The particles are likely to be CuI, cuprous iodide, which is insoluble in water, but should dissolve readily in the presence of ammonia [11]. Addition of NH₃ (aq) was found to dissolve the particles.

The reaction was also performed under nitrogen. Equal volumes (10mL) of copper(II) sulfate (0.0010 M) and potassium iodide (0.0010M) were added to a 100 mL two-necked round bottom flask equipped with a rubber septum and a N₂ inlet. The solution containing copper(II) and iodide had been heated on a hot water bath (35-40 °C) for 10 minutes. Using a syringe, 10 mL borohydride was added while swirling the flask. The reaction was kept under nitrogen. The spectrum was taken within a minutes after the color appeared. The color and plasmon absorbance are similar to those of the reactions performed open to the air, except that yellow copper colloidal remains stable for a day. Gradually oxidation of copper particles takes place with disappearance of the plasmon peak and formation of yellow particles. The sample prepared for AFM and TEM characterization was prepared in this way.
4.5.3 Results and Discussion

To determine optimal conditions for synthesis of stable copper NPs via borohydride reduction of copper(II) salts in presence of iodide, the following were varied and results are summarized in Tables 4.6 and 4.7:

- Relative molarities of reactants
- Use of additives
- Temperature
- Order of addition of reagents

The Table 4.6 is sorted according to increasing stability of copper nanoparticles sol. Except for samples 1-5, all the reactions produced copper NPs with the typical plasmon peak (560 nm) in their visible spectra. If red color doesn’t appear, there is no plasmon resonance (SPR), there is no product and of course, stability cannot be recorded. Relative number of moles and molarity are
the same for every entry in Table 4.6. Samples were prepared according the procedure in Section 4.5.2.

**Table 4.6.** Addition of borohydride to the mixture of copper sulfate (0.0010 M) and iodide under varying conditions. Samples were kept in closed vials at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\frac{[\text{BH}_4^-]}{[\text{Cu}^{2+}]}$</th>
<th>Additive mol/L</th>
<th>$^a$Rxn time, min color</th>
<th>$^b$Stability time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>KI, 0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>KI, 0.001</td>
<td>90, Orange</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6.0</td>
<td>KI, 0.020</td>
<td>90, Orange</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6.0</td>
<td>KI, 0.010</td>
<td>40, Red</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>6.0</td>
<td>KI, 0.005</td>
<td>30, Red</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>6.0</td>
<td></td>
<td>10-20, Red</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>6.0</td>
<td>NaCl, 0.001</td>
<td>10-20, Red</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>4.0</td>
<td>KI, 0.001</td>
<td>10-20, red</td>
<td>40</td>
</tr>
<tr>
<td>9</td>
<td>6.0</td>
<td>KBr, 0.001</td>
<td>10-20, Red</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>6.0</td>
<td>KI, 0.0001</td>
<td>10-20, Red</td>
<td>45</td>
</tr>
<tr>
<td>11</td>
<td>5.0</td>
<td>KI, 0.001</td>
<td>10-20, Red</td>
<td>60</td>
</tr>
<tr>
<td>12</td>
<td>6.0</td>
<td>KI, 0.002</td>
<td>30, Red</td>
<td>120</td>
</tr>
<tr>
<td>13</td>
<td>6.0</td>
<td>KI, 0.001</td>
<td>10-20, Red</td>
<td>180</td>
</tr>
<tr>
<td>14</td>
<td>10</td>
<td>KI, 0.001</td>
<td>10-20, Red</td>
<td>180</td>
</tr>
<tr>
<td>15</td>
<td>6.0</td>
<td>NaI, 0.001</td>
<td>10-20, Red</td>
<td>180</td>
</tr>
<tr>
<td>16</td>
<td>6.0</td>
<td>NH$_4$I, 0.001</td>
<td>10-20, Red</td>
<td>180</td>
</tr>
<tr>
<td>17</td>
<td>20</td>
<td>KI, 0.001</td>
<td>40, Red</td>
<td>240</td>
</tr>
</tbody>
</table>

$^a$, $^b$The data is average of three readings, with error of about ±10%.
4.5.3.1 Relative Molarities of Reactants

From Table 4.6 arranged according to increasing stability, it can be seen that certain conditions produce products with lower stability (less than 100 min). Relevant samples are indicated for each condition.

As in previous borohydride reduction (Section 4.4) there is no product when the molar ratio of borohydride to copper salt is less than 2 to 1, the stoichiometric requirement and stability improves as the concentration ratio is increased above 6 to 1 ratio. When the ratio is below 6 to 1 the stability time decreases as in samples 1, 8, and 11. For BH$_4^-$:Cu$^{2+}$ 30:1 mole ratio plasmon absorbance did not appear and the color of solution was orange (Sample 2). It is possible that excess borohydride stabilizes the product and is required in lesser amounts in the presence of iodide.

- Iodide is needed to improve stability as in samples 6 (no halide), 7 (chloride) and 9 (bromide).
- The concentration of iodide cannot be $< 0.001$ M as in sample 10 (0.0001).
- Very large ionic concentration also interferes with stability, that is, when $[\Gamma] > 0.002$ M as in samples 5 (0.005), 4 (0.01), 3 (0.02).
4.5.3.2 Temperature Effect

All the samples in Table 4.6 were prepared according the procedure in Section 4.5.2 with copper(II)/I\(^-\) heated on a hot water bath at 35-40 °C. In addition, two samples with BH\(_4\):Cu\(^{2+}\) mole ratios of 6:1 and 10:1 were prepared at room temperature. The reaction time decreases but the stability of copper nanoparticles is not decreased at the higher temperature (35-40 °C). The red color appeared in 30-45 min for samples (mole ratio 6:1 and 10:1) prepared at room temperature, compared to 10-20 min for the samples (mole ratio 6:1 and 10:1) prepared at 35-40 °C. The stability time was 180 min for both samples prepared at the room temperature and at 35-40 °C. The effect of temperature on the reaction time was explained in borohydride reduction method, Section 4.4.3.3

4.5.3.3 Order of Addition of Reagents

All the reactions in Table 4.6 were prepared by addition of borohydride to the mixture of copper(II) and iodide solution. Experiments were also carried out by changing the order of addition of reagents;

1) borohydride was added to the mixture of copper(II) and iodide solutions.
2) copper(II) was added to the mixture of borohydride and iodide solutions.
3) iodide was added to the mixture of copper(II) and borohydride.

The results are summarized in Table 4.7. The plasmon absorbance is not visible for Sample 3. Addition of copper(II) to the BH\(_4\)/I\(^-\) mixture increases the reaction time but does not increase the stability (Sample 2).
Table 4.7. Effect of order of addition using equal volumes of 0.0060 M borohydride, 0.0010M copper sulfate and 0.0010M potassium iodide mixed at 35-40 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Order of addition of reagents</th>
<th>aRxn time, min and color</th>
<th>bStability time min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BH$_4^-$ to (Cu$^{2+}$ + I$^-$)</td>
<td>10-20, Red</td>
<td>120-180</td>
</tr>
<tr>
<td>2</td>
<td>Cu$^{2+}$ to (BH$_4^-$ + I$^-$)</td>
<td>60, Red</td>
<td>120</td>
</tr>
<tr>
<td>3</td>
<td>I$^-$ to (Cu$^{2+}$ + BH$_4^-$)</td>
<td>Orange</td>
<td></td>
</tr>
</tbody>
</table>

a, bThe data is average of three readings, with error of about ±10%.

4.5.4 Characterization of Copper Nanoparticles Prepared via Borohydride Reduction with Iodide

Copper NPs were examined using UV-VIS spectroscopy, AFM and TEM.

4.5.4.1 Optical Characterization

Copper nanoparticles were produced from a reaction in which 0.0010 M copper sulfate was reduced using sodium borohydride with the addition of potassium iodide in a molar ratio of 1 to 6 to 1 (Sample 13 in Table 4.6). Sodium borohydride was added to the mixture of copper sulfate and potassium iodide that had been heated on a hot water bath (35-40 °C) for 10 minutes. The color of solution upon mixing sodium borohydride, copper(II) solution and iodide turns first yellow, then orange, and finally red (Figure 4.5). The spectrum of the clear red colloidal copper product (Figure 4.8a) is shown in Figure 4.9, the plasmon absorbance is at 564 nm. Upon aggregation the color changes from red to yellow.
(Figure 4.8b) and ultimately yellow particles (Figure 4.8c) appear (See Section 4.5.2).

![Graph showing absorption spectrum](image)

**Figure 4.9.** UV–VIS absorption spectrum of red colloidal Cu ($\lambda_{\text{max}} = 564$ nm) which was prepared by the method in Section 4.5.2 and with the Cu$^{2+}$:BH$_4^-$:I$^-$ mole ratio of 1:6:1.

### 4.5.4.2 Particle Size Measurement Using TEM and AFM

The copper nanoparticles that produced the spectrum in Figure 4.9 ($\lambda_{\text{max}} = 564$ nm) were examined using a transmission electron microscope and an atomic force microscope. A sample of copper nanoparticles from the freshly synthesized sol was prepared by drying a small drop on a carbon coated 200 mesh copper grid. The particles were characterized using transmission electron microscopy. The
TEM image of a region of the sample is shown in Figure 4.10, and the size distribution in Figure 4.11. The particle size for this sample is 18 ± 2 nm.

AFM measurements were run on a sample prepared according to Section 4.5.2 and with Cu$^{2+}$:BH$_4^-$:I$^-$ mole ratio of 1:6:1. An AFM sample of copper nanoparticles was prepared by drying 15-20 µL of a freshly synthesized clear red sol on a 9.9 mm mica disc. The AFM image of one region of the sample is shown in Figure 4.12, and the size distribution is shown in Figure 4.13. The particle size for this sample is 20 ± 2 nm. As it was explained in Section 1.3 measurements of particle height by AFM correspond reasonably well with diameter of particles measured by TEM.

Figure 4.10. The TEM image of Cu NPs that were prepared by the method in Section 4.5.2 and with the Cu$^{2+}$:BH$_4^-$:I$^-$ mole ratio of 1:6:1. The size bar is 20 nm.
**Figure 4.11.** TEM-derived Cu nanoparticle size distribution.

**Figure 4.12.** a) (5.39 µm x 5.39 µm) AFM image of Cu nanoparticles which was prepared by the method in Section 4.5.2 and with the Cu^{2+}:BH_4⁻:I⁻ mole ratio of 1:6:1.
Figure 4.13. Size distribution of colloidal Cu dispersion derived by AFM.

Mean = 20 ± 2 nm
SD = 4.3
Count = 161
4.6 Synthesis of Copper Nanoparticles by Reduction with Isopropyl Alcohol in Presence of CTAB

The synthesis method by reduction with isopropyl alcohol in presence of cetyltrimethylammonium bromide (CTAB), the protocol, results, discussion and characterization of copper nanoparticles with UV-Visible spectroscopy and AFM are presented in this section.

4.6.1 Synthesis Method

Alcohols have been used as reducing agents at elevated temperatures in synthesis of metal nanoparticles [13, 14]. In this work copper(II) nitrate is mixed with a solution of isopropyl alcohol (IPA) and cetyltrimethylammonium bromide (CTAB) (Figure 4.14) at room temperature. CTAB molecules catalyze the reduction of Cu$^{2+}$ ions to Cu$^{0}$ with IPA. CTAB also acts as a capping agent by surrounding the surface of copper nanoparticles. The long chain cetyl groups stabilize the NPs and prevent aggregation [15].

The chemical reaction is the reduction of copper(II) nitrate with isopropyl alcohol:

$$Cu^{2+} + CH_3-CH(OH)-CH_3 \rightarrow Cu + (CH_3)_2C=O + 2H^+$$

The method produces 20 nm particles as determined from AFM. The plasmon absorbance is near 560 nm.
Figure 4.14. The structure of cetyltrimethylammonium bormide (CTAB).

4.6.2 Protocol

Reactions were done in clean dry 125-mL Erlenmeyer flasks open to the air. In a typical reaction, a 10-mL volume of 0.0030M copper nitrate prepared in IPA solution is added drop wise (about 1 drop/second) to 0.090 M of CTAB/IPA solution. The reaction mixture was stirred vigorously on a magnetic stir plate. The solution turned violet after the addition of 2 mL of copper nitrate (Figure 4.15b), darker violet after addition of 5 ml copper nitrate and dark violet (Figure 4.15a) when the entire volume of copper nitrate had been added.

The appearance of a violet color indicated the presence of copper nanoparticles. The plasmon absorbance near 560 nm was present in a spectrum taken within minutes after the color appeared (Figure 4.16b). The product, stored in a closed vial was stable for a week. After one week the violet color and plasmon band started to vanish.
Figure 4.15. (a) Freshly prepared dark violet Cu sol, and (b) violet solution.

4.6.3 Results and Discussion

To determine optimal conditions for synthesis of stable copper NPs with isopropyl alcohol in presence of CTAB, the following were varied and results are summarized in Tables 4.8-4.11:

- Relative molarities of reactants
- Relative moles of reactants
- Order of addition of copper and CTAB solutions
- Stirring
- Temperature
- Solvent

Tables 4.8 to 4.11 were sorted according to increasing $\lambda_{\text{max}}$. 
4.6.3.1 Relative Molarities of Reactants and Relative Moles of Reactants

To find the optimum molar ratios of reactants several experiments were performed:

1) Varying the Copper(II) Nitrate Volume and Keeping the CTAB Volume Constant

Copper(II) solution (0.0030 M) from 1 mL to 30 mL was added drop wise to 10 mL of 0.090 M CTAB/IPA. The results are summarized in Table 4.8.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu(II) Vol. mL</th>
<th>mol CTAB mol Cu$^{2+}$</th>
<th>$\lambda_{max}$ nm</th>
<th>Shoulder at 630 nm</th>
<th>Abs. at 800 nm</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>300</td>
<td>534</td>
<td>√</td>
<td></td>
<td>Violet</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>150</td>
<td>534</td>
<td>√</td>
<td></td>
<td>Violet</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>100</td>
<td>534</td>
<td>√</td>
<td></td>
<td>Violet</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>75</td>
<td>534</td>
<td>√</td>
<td></td>
<td>Violet</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>60</td>
<td>545</td>
<td>√</td>
<td></td>
<td>Darker Violet</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>50</td>
<td>551</td>
<td>√</td>
<td></td>
<td>Darker Violet</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>43</td>
<td>551</td>
<td>√</td>
<td></td>
<td>Darker Violet</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>38</td>
<td>551</td>
<td></td>
<td></td>
<td>Darker Violet</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>33</td>
<td>553</td>
<td></td>
<td></td>
<td>Dark Violet</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>30</td>
<td>556</td>
<td></td>
<td></td>
<td>Dark Violet</td>
</tr>
<tr>
<td>11</td>
<td>15</td>
<td>20</td>
<td>560</td>
<td>√</td>
<td></td>
<td>Violet-green</td>
</tr>
<tr>
<td>12</td>
<td>20</td>
<td>15</td>
<td>564</td>
<td>√</td>
<td></td>
<td>Violet-green</td>
</tr>
<tr>
<td>13</td>
<td>25</td>
<td>12</td>
<td>570</td>
<td>√</td>
<td></td>
<td>Greenish</td>
</tr>
<tr>
<td>14</td>
<td>30</td>
<td>10</td>
<td>570</td>
<td>√</td>
<td></td>
<td>Greenish</td>
</tr>
</tbody>
</table>
The results in Tables 4.8 indicate that as the CTAB:Cu\textsuperscript{2+} mole ratio reduces from 300:1 (Sample 1) to 10:1 (Sample 14), the plasmon absorbance shifts to a longer wavelength (570nm) and the color is changed from violet to greenish. Also, at CTAB:Cu\textsuperscript{2+} mole ratios >40, a shoulder near 630 nm appears which may be related to the formation of the particle shapes other than spheres, such as decahedral nanocrystals and trigonal prism [9] (See Section 4.6.4.1).

In addition, as the CTAB:Cu\textsuperscript{2+} mole ratio reduces from 30:1 to 10:1, absorbance at 800 nm increases. One explanation for appearance of the peak at 800 nm is that, at lower mole ratios, e.g., 10:1, there are 10 CTAB per copper(II) ion and after the complete addition some copper(II) ions remain unreacted, which can be observed by the appearance of absorption at 800nm [15]. An other explanation is that when copper particles are surrounded by an oxide layer, a peak appears at about 570 nm while a residual absorption characteristic of copper oxide at 800 nm is also observed [8, 9, 16]. Figure 4.17 shows the spectra of reactions from mole ratios 75:1, 30:1, and 10:1. A shoulder at 630 nm is observed for the mole ratio 75:1 and an absorbance at 800 nm is observed for the mole ratio 10:1.

The absorption spectrum obtained at CTAB:Cu\textsuperscript{2+} mole ratio 30:1 with plasmon peak near 560 nm shows no residual absorption at 800 nm, and no shoulder at 630 nm suggesting formation of pure copper nanoparticles.
Figure 4.16. UV–VIS absorption spectra of violet solution where CTAB:Cu$^{2+}$ mole ratio is (a) 75:1 ($\lambda_{\text{max}} = 534$ nm), (b) 30:1 ($\lambda_{\text{max}} = 556$ nm), and (c) 10:1 ($\lambda_{\text{max}} = 570$ nm).

2) Varying the CTAB Volume and Keeping the Copper(II) Volume Constant

The CTAB volumes were changed from 10 to 40 mL and copper(II) volume was kept constant (10 mL). Copper(II) (0.0030 M) was added drop wise to CTAB/IPA (0.090 M). The results are summarized in Table 4.9.
**Table 4.9.** Addition of Cu(NO$_3$)$_2$·2.5H$_2$O to 10 mL to 40 mL CTAB/IPA with various CTAB: Cu$^{2+}$ mole ratios. Reactions were carried out at room temperature. The samples were stable for a week.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CTAB Vol. mL</th>
<th>mol CTAB/mol Cu$^{2+}$</th>
<th>$\lambda_{\text{max}}$ nm</th>
<th>Shoulder at 630 nm</th>
<th>Abs. at 800 nm</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>120</td>
<td>534</td>
<td>$\sqrt{\text{v}}$</td>
<td></td>
<td>Violet</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>90</td>
<td>535</td>
<td>$\sqrt{\text{v}}$</td>
<td></td>
<td>Violet</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>60</td>
<td>543</td>
<td></td>
<td></td>
<td>Dark violet</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>30</td>
<td>563</td>
<td></td>
<td></td>
<td>Dark violet</td>
</tr>
</tbody>
</table>

The shoulder at 630 nm was again observed for the higher CTAB:Cu$^{2+}$ mole ratios (90:1 and 120:1); See Part (1).

**3) Varying the CTAB Concentration and Keeping the Copper(II) Concentration Constant**

A fixed concentration of copper(II) (0.0030 M) was added to CTAB/IPA solutions containing varying concentrations of CTAB in IPA. The volumes of the copper nitrate and CTAB were kept constant. The results are summarized in Table 4.10.
Table 4.10. Alcohol (IPA) reduction of Cu(NO₃)₂·2.5H₂O with various concentrations of CTAB. Reactions were carried out at room temperature. The samples were stable for a week.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[CTAB] mol/L</th>
<th>mol CTAB mol Cu²⁺</th>
<th>λₘₐₓ nm</th>
<th>Abs.</th>
<th>Abs. at 800 nm</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00075</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td>Blue</td>
</tr>
<tr>
<td>2</td>
<td>0.003</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>Yellow</td>
</tr>
<tr>
<td>3</td>
<td>0.090</td>
<td>30</td>
<td>556</td>
<td>0.807</td>
<td></td>
<td>Dark Violet</td>
</tr>
<tr>
<td>4</td>
<td>0.075</td>
<td>25</td>
<td>564</td>
<td>0.694</td>
<td></td>
<td>Violet</td>
</tr>
<tr>
<td>5</td>
<td>0.060</td>
<td>20</td>
<td>566</td>
<td>0.562</td>
<td>√</td>
<td>Violet-green</td>
</tr>
<tr>
<td>6</td>
<td>0.045</td>
<td>15</td>
<td>570</td>
<td>0.489</td>
<td>√</td>
<td>Violet-green</td>
</tr>
<tr>
<td>7</td>
<td>0.030</td>
<td>10</td>
<td>572</td>
<td>0.324</td>
<td>√</td>
<td>Greenish</td>
</tr>
</tbody>
</table>

Similar to the results in Table 4.8, as the CTAB:Cu⁺² mole ratio reduces from 30:1 (Sample 3) to 10:1 (Sample 7), plasmon absorbance shifts to longer wavelength (570nm), the intensity of the peak also decreases, a peak appears at 800 nm, and the color of solution changes from dark violet to greenish (Figure 4.17).
4.6.3.2 Order of Addition of Copper and CTAB Solutions

The order of addition of the reagents was examined. The CTAB/IPA (0.090 M) from 2 mL to 10 mL was added to 10 mL of copper(II)/IPA solution (0.0030 M). On reversing the sequence of addition, the results obtained are different (Table 4.11). The $\lambda_{\text{max}}$ can be observed only after addition of a large amount (10 mL) of CTAB (Sample 5). When copper(II) is added to CTAB/IPA solution, copper(II) ions are being introduced in an excess of CTAB facilitating immediate reduction of Cu$^{2+}$ ions to Cu$^0$. Addition of CTAB/IPA to Cu(II)/IPA solution, may lead to an incomplete conversion of Cu$^{2+}$ ions to Cu$^0$ [15].
Table 4.11. Effect of order of addition of reagents. Various volumes of CTAB/IPA were added to Cu(NO₃)₂·2.5H₂O. Reactions were carried out at room temperature. The samples were stable for a week.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[CTAB] mol/L</th>
<th>Volume of CTAB mL</th>
<th>mol CTAB mol Cu²⁺</th>
<th>λ max nm</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.090</td>
<td>2</td>
<td>6</td>
<td></td>
<td>Green-brown</td>
</tr>
<tr>
<td>2</td>
<td>0.090</td>
<td>4</td>
<td>12</td>
<td></td>
<td>Green-brown</td>
</tr>
<tr>
<td>3</td>
<td>0.090</td>
<td>6</td>
<td>18</td>
<td></td>
<td>Green-brown</td>
</tr>
<tr>
<td>4</td>
<td>0.090</td>
<td>8</td>
<td>24</td>
<td></td>
<td>Green-brown</td>
</tr>
<tr>
<td>5</td>
<td>0.090</td>
<td>10</td>
<td>30</td>
<td>553</td>
<td>Dark violet</td>
</tr>
</tbody>
</table>

4.6.3.1 Effect of Other Conditions

The effects of stirring, choice of solvent and temperature were studied.

Stirring

All the reaction mixtures in Table 4.8 were stirred vigorously on a magnetic stir plate (See Section 4.6.2) except that four samples of mole ratios 60, 38, 30, and 15 were also prepared by adding the copper nitrate in several parts to CTAB/IPA while swirling the flask. No change in λ max was observed compared to the procedure typically used when the reaction mixture was stirred with a magnet bar.
Solvent

The synthesis of copper NPs was also carried out in aqueous medium as well as in water:IPA in 1:1 ratio by volume. In both cases, the plasmon absorbance was not observed and the solutions remained colorless which indicates that copper NPs were not formed. Thus, it can be concluded that the solvent used (IPA) plays a crucial role in effective reduction of Cu$^{2+}$ to Cu$^0$.

Temperature

The temperature has a significant effect on stability of copper nanoparticles. It was observed when the room temperature was 20-23 °C, after completion of the reaction violet particles (whiskers like) appeared in solutions in one hour. The CTAB/IPA solution was heated on a hot water bath at 28-30 °C for 10 min, and then the reaction was performed with heated CTAB in IPA. After completion of the reaction a brownish-red solution was observed, plasmon absorbance was less pronounced and black particles appeared in the solution after about 6 hrs. The spectrum of the brown-red solution is shown in Figure 4.18.

Copper(II) was also added to the CTAB/IPA solution (CTAB:Cu$^{2+}$ mole ratio of 30:1) that had been heated on a hot water bath at 26-28 °C. No change in plasmon absorbance and stability of copper colloid was observed at this temperature compared to the procedure typically used when the reaction was performed at room temperature of about 25 °C.
Figure 4.18. UV–VIS absorption spectrum of the brownish-red solution that was prepared at 28-30 °C and with CTAB:Cu²⁺ mole ratio of 30:1.

4.6.4 Characterization of Copper Nanoparticles Prepared via Isopropyl Reduction with CTAB

Copper nanoparticles were characterized using UV-VIS spectroscopy, AFM and TEM.

4.6.4.1 Optical Characterization

The plasmon absorbance appears in all samples in Tables 4.8-4.10 between 535 and 560 nm. A shoulder at about 630 nm is present in those with the highest molar ratios of CTAB to Cu (300:1 to 43:1, Samples 1-7 in Table 4.8). The absorption spectrum near 560 nm is related to the plasmon band of spherical copper particles. The absorption at 630 nm could be due to the presence of other...
particle shapes, such as decahedral nanocrystals, trigonal prisms and ellipsoidal particles [9].

At lower CTAB:Cu\(^{2+}\) mole ratios, 20:1 to 10:1, a residual absorbance can be observed at \(~800\, \text{nm}\) which is typical for Cu\(^{2+}\). Furthermore, the absorbance at 800 nm could be due to the formation of an oxide monolayer [8, 9, 16] (See Section 4.6.3.1). The absorption spectra obtained at 38:1, 33:1, 30:1 mole ratios show no residual absorbance at 800 nm and no shoulder at 630 nm. Among these mole ratios, the characteristic plasmon absorbance (\(~560\, \text{nm}\)) was observed for CTAB:Cu\(^{2+}\) 30:1 mole ratio (Figure 4.19).

![Absorption Spectrum](image)

**Figure 4.19.** UV–VIS absorption spectrum of dark violet colloidal Cu (\(\lambda_{\text{max}} = 556\, \text{nm}\)) that was prepared by the method in Section 4.6.2 and with CTAB: Cu\(^{2+}\) mole ratio of 30 to 1.
4.6.4.2 Particle Size Measurement Using AFM

Copper nanoparticles that produced the spectrum in Figure 4.19 were characterized using atomic force microscopy. A sample of copper nanoparticles was prepared by drying 15-20 µL of a freshly synthesized dark violet sol on a 9.9 mm mica disc. The AFM image of a region of the sample is shown in Figure 4.20, and the size distribution is shown in Figure 4.21. The AFM image and size distribution show the copper particles are polydisperse with mean size of 20 nm.

![AFM Image](image)

**Figure 4.20.** (5.43 μm x 5.43 μm) AFM image of Cu nanoparticles that was prepared by the method in sections 4.6.2 and with CTAB:Cu\(^{2+}\) mole ratio of 30:1.
4.6.5 Stability of Copper Nanoparticles

Stability of copper NPs was investigated by observing the time dependence of the absorption spectra of the copper sols prepared by the method in Section 4.6.2. Five samples of CTAB:Cu$^{2+}$ of mole ratios of 75:1, 50:1, 30:1, 20:1, and 12:1 were stored at room temperature and UV-VIS spectra of the samples were taken after three hours, twelve hours, one day (24 hrs), two days (48 hrs), one week (168 hrs), two weeks (336 hrs), and three weeks (504 hrs). The spectra of the sample with the mole ratio 30:1 are shown in Figures 4.22.

The intensity of the absorption band gradually decreases over time and the color of solution becomes less pronounced. There is no obvious difference in the
position of the absorption peak after twelve hours, only a slight reduction in intensity of the peak up to one week. After three weeks, the absorbance dropped significantly as it is seen in Figure 4.22; thus it can be concluded that copper NPs are stable for a week.

**Figure 4.22.** UV – VIS spectra of colloidal copper nanoparticles (CTAB:Cu$^{2+}$ mole ratio 30:1), stored for different lengths of time.
4.7 Synthesis of Copper Nanoparticles by Reduction with Sugar

The synthesis method by reduction with sugar, the protocol, results, discussion and characterization of copper nanoparticles with UV-Visible spectroscopy and AFM are presented in this section.

4.7.1 Synthesis Method

In this method copper nanoparticles were produced using reducing sugars, such as glucose, fructose and lactose, which reduce copper ion to elemental copper [17, 18]. The reaction can be summarized by the equation below in which glucose is oxidized to produce gluconic acid, C₆H₁₂O₇H, which becomes the gluconate ion, C₆H₁₂O₇⁻, in the presence of the base, NaOH (the solvent is distilled water):

\[
\text{Cu}^{2+} + C_6H_{12}O_6 \xrightarrow{\text{H}^+} \text{Cu}^+ + C_6H_{12}O_7^-
\]

Adsorption of negative gluconate ions gives growing copper nanoparticles a negative surface charge. The nanoparticles are kept suspended in water separated from one another by repulsive electrostatic forces.

The method produces a yellowish sol with plasmon absorbance between 462 and 549 nm for the three different sugars. AFM images of copper sols reduced with glucose, fructose and lactose were obtained and the results including the particle sizes are summarized in Table 4.14.
4.2.2 Protocol

Three different solutions were prepared by dissolving 0.2, 0.3, 0.4 g of sugar in 5.0 mL of water. Then, 30 μL of sodium hydroxide (1.0 M) were added to each solution and heated to 50 °C on a hot plate. Finally, 0.2 mL of 0.01 M CuSO$_4$5H$_2$O were added to each solution and the final mixture was heated until a yellow color appeared (3-5 minutes). The spectrum was taken within minutes after the color appeared. The yellowish product, stored in a closed vial, was stable for a few hours. However, once the vial is opened, it takes about 15-30 minutes for aggregation to take place. Upon aggregation, the absorption peak disappears; the yellowish sol becomes colorless, after which yellowish particles form.

The reaction was also performed under nitrogen. Glucose (0.2 g) was dissolved in 5.0 mL of water in a 100 mL two-necked round bottom flask equipped with a rubber septum and a N$_2$ inlet. As above, 30 μL of sodium hydroxide (1.0 M) were added and heated to 50 °C in a hot water bath. Finally, 0.2 mL of 0.01 M CuSO$_4$5H$_2$O were added to the flask thorough a syringe. The reaction was kept under nitrogen. The method above was repeated for 0.3 g and 0.4 g glucose. The color and plasmon absorbance were similar to those of the reactions performed open to the air, except that yellow colloidal copper remained stable for a day. Gradually oxidation of copper particles takes place with disappearance of the absorption peak and formation of yellow particles. The samples prepared for AFM characterization were prepared in this way.
4.7.3 Results and Discussion

To determine optimum sugar concentrations for synthesis of copper nanoparticles, various concentrations were used and results are summarized in Tables 4.12 and 4.13:

The absorption at 800 nm is indicated using numbers from 0 (none) to 5 (the largest).

Table 4.12. Sugar reduction of 0.01 M copper sulfate with various concentrations of sugars. The table is sorted according to increasing $\lambda_{max}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reducing sugar</th>
<th>[sugar] [Cu$^{2+}$]</th>
<th>mol sugar mol Cu$^{2+}$</th>
<th>$\lambda_{max}$ nm</th>
<th>Shoulder at 650 nm</th>
<th>Abs. at 800 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Glucose</td>
<td>44</td>
<td>1000</td>
<td>462</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Glucose</td>
<td>34</td>
<td>800</td>
<td>471</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>Lactose</td>
<td>24</td>
<td>600</td>
<td>475</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>Lactose</td>
<td>18</td>
<td>440</td>
<td>482</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>Fructose</td>
<td>34</td>
<td>800</td>
<td>490</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>Glucose</td>
<td>1</td>
<td>25</td>
<td>501</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>Fructose</td>
<td>44</td>
<td>1000</td>
<td>506</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>8</td>
<td>Glucose</td>
<td>11</td>
<td>275</td>
<td>542</td>
<td>$\sqrt{}$</td>
<td>4</td>
</tr>
<tr>
<td>9</td>
<td>Glucose</td>
<td>22</td>
<td>500</td>
<td>546</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>Lactose</td>
<td>12</td>
<td>300</td>
<td>549</td>
<td>$\sqrt{}$</td>
<td>4</td>
</tr>
<tr>
<td>11</td>
<td>Fructose</td>
<td>22</td>
<td>500</td>
<td>575</td>
<td>$\sqrt{}$</td>
<td>4</td>
</tr>
</tbody>
</table>
Table 4.13. Glucose reduction of 0.01 M copper sulfate. The table is sorted according to decreasing mol sugar/mol Cu^{2+}.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Sugar]</th>
<th>mol sugar</th>
<th>λmax</th>
<th>Shoulder</th>
<th>Abs. at</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Cu^{2+}]</td>
<td>mol Cu^{2+}</td>
<td>nm</td>
<td>at 650 nm</td>
<td>800 nm</td>
<td>time, hrs</td>
</tr>
<tr>
<td>1</td>
<td>44</td>
<td>1000</td>
<td>462</td>
<td>0</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>34</td>
<td>800</td>
<td>471</td>
<td>1</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>22</td>
<td>500</td>
<td>546</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>275</td>
<td>542</td>
<td>√</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>25</td>
<td>501</td>
<td>5</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>

As the glucose:Cu^{2+} mole ratio is reduced from 1000:1 to 500:1, the plasmon absorbance shifts to longer wavelengths and the absorption at 800 nm increases (Table 4.13). A shoulder near 650 nm appears for the product of the mole ratio 275:1 (Figure 4.23).

At the mole ratio 25:1 (Sample 5) the absorption peak at 501 nm is disappearing and the absorbance at 800 nm increases significantly (Figure 4.24). In this case there is not enough glucose to stabilize the nanoparticles. In addition, as already discussed with the alcohol/CTAB reduction method (Section 4.6.3), at lower mole ratios there is less glucose with respect to copper ions, so that some copper(II) remains unreacted and the absorption at 800 nm increases. In contrast, at the highest mole ratio 1000:1, a well-defined absorption spectrum is observed.
with a plasmon peak centered at 462 nm and no absorption at 800 nm (Figure 4.25). This indicates the formation of pure copper nanoparticles.

The color of the mixtures were dark yellow after the completion of the reaction for all the samples in Table 4.13 except for #5 (mole ratio 25:1) which was light yellow. Copper nanoparticle sols were stable for a few hours in all cases except for the mole ratio 25:1 in which the color and the absorption peak disappeared after 30 minutes.

![UV–VIS spectrum of Sample 4 (Table 4.14) (λ_max =542 nm).](image)

**Figure 4.23.** UV–VIS spectrum of Sample 4 (Table 4.14) (λ_max =542 nm).
**Figure 4.24.** UV–VIS absorption spectrum of the light yellow solution where glucose:Cu$^{2+}$ mole ratio is 25:1.
Figure 4.25. UV–VIS absorption spectrum of copper sol ($\lambda_{\text{max}} = 462$ nm) which was prepared by the method in Section 4.2.2 and with glucose:Cu$^{2+}$ mole ratio of 1000:1.

4.7.4 Particle Size Measurement Using AFM

Optical properties of copper nanoparticles sols were discussed above (Section 4.7.3). AFM of almost all samples in Table 4.12 were taken and particles sizes are listed in Table 4.14. An AFM sample of copper nanoparticles was prepared by drying 15-20 $\mu$L of a freshly synthesized clear yellow sol on a 9.9 mm mica disc. The AFM image of one region of Sample 6 (Table 4.14) is shown in Figure 4.26 and size distribution of the above sample is shown in Figure 4.27.
The AFM images and size distribution show the copper particles are polydisperse in all cases. Particle sizes are smaller for higher sugar:Cu\(^{2+}\) mole ratio, e.g., 25 nm particles for fructose:Cu\(^{2+}\) 1000:1 mole ratio (Sample 8) compared to 35 nm particles for fructose:Cu\(^{2+}\) 500:1 mole ratio (Sample 10), See Table 4.14.

**Table 4.14.** Size of copper particles. The table is sorted according to increasing of the particle size.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reducing sugar</th>
<th>(\frac{\text{mol sugar}}{\text{mol Cu}^{2+}})</th>
<th>(\lambda_{\text{max}}) nm</th>
<th>Particle Size nm</th>
<th>SD</th>
<th>Count</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lactose</td>
<td>440</td>
<td>482</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Glucose</td>
<td>25</td>
<td>501</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Glucose</td>
<td>275</td>
<td>542</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Lactose</td>
<td>600</td>
<td>475</td>
<td>15</td>
<td>6.5</td>
<td>19</td>
</tr>
<tr>
<td>5</td>
<td>Glucose</td>
<td>800</td>
<td>471</td>
<td>16</td>
<td>3.9</td>
<td>11</td>
</tr>
<tr>
<td>6</td>
<td>Glucose</td>
<td>1000</td>
<td>462</td>
<td>19</td>
<td>8.2</td>
<td>44</td>
</tr>
<tr>
<td>7</td>
<td>Glucose</td>
<td>500</td>
<td>546</td>
<td>22</td>
<td>11.7</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>Fructose</td>
<td>1000</td>
<td>506</td>
<td>25</td>
<td>6.9</td>
<td>36</td>
</tr>
<tr>
<td>9</td>
<td>Lactose</td>
<td>300</td>
<td>549</td>
<td>29</td>
<td>7.5</td>
<td>19</td>
</tr>
<tr>
<td>10</td>
<td>Fructose</td>
<td>500</td>
<td>575</td>
<td>35</td>
<td>10.4</td>
<td>20</td>
</tr>
<tr>
<td>11</td>
<td>Fructose</td>
<td>800</td>
<td>490</td>
<td>47</td>
<td>14.5</td>
<td>25</td>
</tr>
</tbody>
</table>
**Figure 4.26.** a) (21.6 µm x 21.6 µm) AFM image of Cu nanoparticle (Sample 6 in Table 4.15), b) close up of a region of the AFM image from part (a).

**Figure 4.27.** Size distribution of colloidal Cu dispersion derived by AFM.
4.7.5 Synthesis of Copper Nanoparticles Using Household Chemicals

The synthesis method for making colloidal copper from household materials, results and discussion will be presented in the section. The final lab documentation on synthesis of copper nanoparticles from household chemicals using simple equipment will be presented in Appendix B [19].

4.7.5.1 Synthesis Method

In this experiment copper sulfate pentahydrate from root killer provides copper(II) ions. The reducing agent is glucose from tablets, taken to raise low blood sugar. The reaction used is described in Section 4.7.1. The tablets contain ingredients in addition to glucose (Table 4.15) which are listed on the label in order from highest to lowest amounts. The identity of the ingredients depends on the brand of tablet.
Table 4.15. Ingredients in glucose tablets.

<table>
<thead>
<tr>
<th>Ingredients in glucose tablets</th>
<th>Formula</th>
<th>Solubility in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascorbic Acid</td>
<td>C_6H_8O_6</td>
<td>Soluble</td>
</tr>
<tr>
<td>Carageenan</td>
<td>a polysaccharide</td>
<td>Soluble</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>C_6H_8O_7</td>
<td>Soluble</td>
</tr>
<tr>
<td>Maltodextrin</td>
<td>(C_{12}H_{20}O_{10})_n</td>
<td>Soluble</td>
</tr>
<tr>
<td>Xylitol</td>
<td>C_3H_12O_5</td>
<td>Soluble</td>
</tr>
<tr>
<td>Yellow No. 6</td>
<td>C_{16}H_{12}N_2O_7S_{2.2}Na</td>
<td>Soluble</td>
</tr>
<tr>
<td>Cellulose</td>
<td>(C_{6}H_{10}O_{5})_n</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Magnesium Stearate</td>
<td>C_{36}H_{70}MgO_4</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>C_{18}H_{36}O_2</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>

4.7.5.2 Protocol

The procedure used is similar to the one described in Section 4.7.1. Liquids were delivered using a disposable pipet, calibrated by adding 40 drops of water to a tared beaker to find the volume of each drop. A segment of a glucose tablet weighing 0.8 g was dissolved in 10 mL distilled water in a 50 mL beaker. The solution was filtered by gravity to remove insoluble substances such as magnesium stearate used to make the tablets. Two drops of 1.0 M NaOH was added with a disposable pipet. The solution was heated to 50 °C on a hot plate.
and 14 drops of 0.010M CuSO₄·5H₂O were added. The solution was heated until a yellow color appeared (3-5 minutes) as in Section 4.7.1.

The yellow appeared only with the BD brand of glucose. There was no color change with Walgreens, Dex and Rite-Aid. Upon examination of the ingredients in Table 4.16, it was realized that the interfering reagent was most likely to be citric acid, since citric acid is the last ingredient listed for BD. Citric acid is one of the ingredients found in glucose tablets in varying amounts. The Becton, Dickinson and Company (BD) provided the amount of citric acid in each tablet (18 mg ± 10%). Other companies refused to give amounts in their products. Citric acid is a chelating agent and its binding to copper(II) has been documented in the literature [20-25].

To test the idea that citric acid inhibits the formation of copper NPs, citric acid was added to reaction mixtures using pure reagent glucose and also glucose tablets.
Table 4.16. Ingredients in various brands of glucose tablets in the order listed on the label.

<table>
<thead>
<tr>
<th>Glucose tablets</th>
<th>Ingredients as listed on the labels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Walgreens</td>
<td>Dextrose, Cellulose, Maltodextrin, Citric Acid, Magnesium Stearate, Orange Flavor, Ascorbic Acid, Yellow No. 6 Lake</td>
</tr>
<tr>
<td>Dex</td>
<td>Dextrose, Cellulose, Maltodextrin, Citric Acid, Magnesium Stearate, Orange Flavor, Ascorbic Acid, Yellow No. 6 Lake</td>
</tr>
<tr>
<td>BD</td>
<td>Dextrose (glucose), Xylitol, Carageenan, Stearic Acid, Magnesium Stearate, Natural &amp; Artificial Flavors, No Preservatives, Citric Acid</td>
</tr>
<tr>
<td>Rite-Aid</td>
<td>Dextrose (Glucose), Citric Acid, Orange Flavor, Magnesium Stearate, Ascorbic Acid, Color (FD&amp;C Yellow 6), Stearic Acid</td>
</tr>
</tbody>
</table>

4.7.5.3 Results and Discussion

To test the idea that citric acid inhibits the formation of Cu NPs, citric acid was added to a reaction mixture using pure reagent glucose. The time required for a color change increases in the presence of excess citric acid, possibly because the copper(II) is depleted. BD brand glucose tablets are likely to contain much less citric acid than Dex tablets since citric acid is the last ingredient listed for BD tablets and the 4th for Dex (See Table 4.16).

In addition, Walgreens, Dex and Rite-Aid glucose tablets contain ascorbic acid, an ingredient that is not in BD tablets. To test the idea that ascorbic acid inhibits the formation of copper nanoparticles, the ascorbic acid was added to the reaction mixture using BD tablets. The solution turned yellow color in 3-5 min.
The presence of ascorbic acid did not inhibit the formation of copper nanoparticles.

The BD glucose tablets were tested to find the amount of citric acid that affects the formation of copper nanoparticles. Citric acid in the range of 0.0 to 5.0 mg was added to the BD glucose tablets (0.8 g). If the added citric acid was more than 2.0 mg, there was no color change, See Table 4.17 and Figure 4.28.

**Table 4.17:** Reaction time vs. amount of citric acid. The color of solution turned light yellow upon reaction.

<table>
<thead>
<tr>
<th>Citric Acid, mg</th>
<th><em>Reaction time, sec</em></th>
<th><em>Reaction time, min</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10</td>
<td>0.17</td>
</tr>
<tr>
<td>0.3</td>
<td>30</td>
<td>0.5</td>
</tr>
<tr>
<td>0.5</td>
<td>60</td>
<td>1</td>
</tr>
<tr>
<td>0.7</td>
<td>180</td>
<td>3</td>
</tr>
<tr>
<td>1</td>
<td>480</td>
<td>8</td>
</tr>
<tr>
<td>1.2</td>
<td>840</td>
<td>14</td>
</tr>
<tr>
<td>1.5</td>
<td>1080</td>
<td>18</td>
</tr>
<tr>
<td>1.7</td>
<td>1500</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>2220</td>
<td>37</td>
</tr>
</tbody>
</table>

*The data is average of three readings, with error of about ±10%.*
Figure 4.28. Graph of the reaction time (sec) vs. the amount of citric acid.

4.8 Summary

Four chemical reduction methods were used to synthesis copper nanoparticles. For each reaction, the dependence of stability of the copper NPs on reagent concentrations, additives, relative amounts of reducing agent and copper salt, and temperature was explored.

4.8.1 Sodium Borohydride Reduction Method

The sodium borohydride reduction method produces a reddish sol containing 52 nm particles measured by AFM with plasmon absorbance near 560 nm. The AFM results indicate that particles are polydisperse. Longer periods of stability result when the BH$_4^-$:Cu$^{2+}$ mole ratio is increased to 20. Increasing the temperature increases the reaction time but reduces the stability of copper nanoparticles. The copper sol was stable for six hours if stored in a closed vial, however, once the vial was opened; it took 5-15 min for aggregation to take place.
4.8.2 Sodium Borohydride Reduction Method with Potassium Iodide

Sodium borohydride was used with stabilizing potassium iodide for synthesis of copper NPs. This method produces a reddish sol with plasmon absorbance near 560 nm. The copper particles are smaller compared to the method without iodide (Section 4.8.1), 18±2 nm measured by TEM and 20±2 nm measured by AFM. The colloidal copper is stable for about three hours when the BH$_4$⁻:Cu$^{2+}$ 6:1 mole ratio is used with 0.001 M potassium iodide compared to 30 min for the same mole ratio and without potassium iodide. The reaction was also performed under nitrogen. The red copper sol was stable for a day. However, performing an experiment using an inert atmosphere is not very convenient.

4.8.3 Isopropyl Alcohol Reduction Method with CTAB

Isopropyl alcohol as a reducing agent and CTAB as a capping agent were used to synthesize copper NPs. The method produces 20 nm particles determined from AFM. The plasmon absorbance is near 560 nm and the color of the copper sol is violet. Various CTAB: Cu$^{2+}$ concentrations and mole ratios were tested. The mole ratio 30:1 provides an absorption peak at 566 nm with no residual absorption at 800 nm, and no shoulder at 630 nm, confirming formation of pure metal particles. The copper colloid from this synthesis method is relatively stable (up to one week). However, this technique is more sensitive to temperature changes. When the room temperature was in the range of 24-28 °C, stable copper NPs could be formed. Only a slight reduction or increase in temperature would result in aggregation of particles within a short time.
4.8.4 Sugar Reduction Method

Three reducing sugars, glucose, fructose and lactose, were used to reduce \( \text{Cu}^{2+} \) ions to \( \text{Cu}^0 \). The method produces a yellowish sol with plasmon absorbance between 462 and 549 nm for the three sugars. To find the optimum ratio of sugar to copper salt, various concentrations were tested. An excess of sugar is required both to reduce the copper(II) and to stabilize the nanoparticles that form. At the mole ratio 1000:1, a well defined absorption spectrum with a plasmon peak centered at 462 nm and no absorption at 800 nm was observed which indicates the formation of pure metallic particles. The yellowish product, stored in a closed vial was stable for a few hours. The reaction was also performed under nitrogen atmosphere producing copper colloid that remained stable for a day. The AFM images show the copper particles are polydisperse in all cases.

4.8.5 Glucose Tablet Reduction

Glucose tablet was used instead of reagent glucose along with other household chemicals to produce copper nanoparticles. When different brands of glucose tablets were used, it was observed that a yellow colored sol appeared only with the BD tablets. There was no color change with Wallgreens, Dex or Rite-Aid. It was found that the formation of copper nanoparticles was inhibited by the presence of citric acid in glucose tablets. The BD brand glucose tablets contain much less citric acid than Walgreens and Dex brand glucose tablets. Citric acid was the last ingredient listed for BD tablets and the 4th for Walgreens. The
maximum amount of citric acid that did not stop the formation of copper nanoparticles from 1g of glucose was found to be a few milligrams. A laboratory experiment based on this procedure was developed for the General Chemistry course.
References


Chapter 5: Conclusion and Future Work

5.1 Conclusion

Colloidal gold was synthesized by citrate reduction of hydrochloroauric acid, HAuCl₄. Larger gold particles (41 nm) were produced as the volume of citrate was reduced from 1.75 mL to 0.5 mL.

Colloidal silver were synthesized by borohydride reduction of silver nitrate. The plasmon absorbance is near 400 nm, and TEM images show that the particle sizes are about 12 nm. The yellow colloidal silver remains stable for as long as several weeks or months. A laboratory experiment on synthesis of colloidal silver was developed.

Four chemical reduction methods were used to synthesis copper nanoparticles. The sodium borohydride reduction method produces a reddish sol containing 52 nm particles measured by AFM with plasmon absorbance near 560 nm. Longer periods of stability (six hours) result when the BH₄⁻:Cu²⁺ mole ratio is increased to 20.

Sodium borohydride was used with stabilizing potassium iodide for the synthesis of copper NPs. This method produces a reddish sol with plasmon absorbance near 560 nm. The copper particles are 18±2 nm measured by TEM and 20±2 nm measured by AFM. The colloidal copper is stable for about three
hours when the BH$_4^{-}$:Cu$^{2+}$ 6:1 mole ratio is used with 0.001 M potassium iodide compared to 30 min for the same mole ratio and without potassium iodide.

Isopropyl alcohol as a reducing agent and CTAB as a capping agent were used to synthesize copper NPs. The method produces 20 nm particles determined from AFM. The plasmon absorbance is near 560 nm and the color of the copper sol is violet. The mole ratio 30:1 provides an absorption peak at 566 nm with no residual absorption at 800 nm, confirming formation of pure metal particles. The copper colloid from this synthesis method is relatively stable (up to one week).

Three reducing sugars, glucose, fructose and lactose, were used to reduce Cu$^{2+}$ ions to Cu$^{0}$. The method produces a yellowish sol with plasmon absorbance between 462 and 549 nm for the three sugars. At the glucose: Cu$^{2+}$ mole ratio of 1000:1, a well defined absorption spectrum with a plasmon peak centered at 462 nm and no absorption at 800 nm was observed which indicates the formation of pure metallic particles. The yellowish product, stored in a closed vial, was stable for a few hours.

Glucose tablet was used instead of reagent glucose along with other household chemicals to produce copper nanoparticles. The yellow colored sol appeared only with the BD tablets. There was no color change with Wallgreens, Dex or Rite-Aid. It was determined that the formation of copper nanoparticles was inhibited by the presence of citric acid in glucose tablets. A laboratory
experiment on synthesis of copper NPs using household chemicals was developed for general chemistry.

5.2 Future Work

The synthesis of copper nanoparticles as well as silver nanorods and silver monolayers will be studied.

5.2.1 Copper Nanoparticles

The synthesis of copper nanoparticles is still ongoing. The attempt is to develop methods that produce more stable copper NPs. The most promising methods will be further studied by continuing to vary conditions. For example, in borohydride reduction method with iodide, keeping the samples in an ice bath after formation of copper nanoparticles may increase the stability. In borohydride reduction method, various concentrations of PVP may be used to determine the optimal concentration of PVP required stabilizing copper nanoparticles.

New synthetic methods to explore include the use of iodide with other reducing agents, e.g. sugar. All methods will be tested in a nitrogen atmosphere at different temperatures with various concentrations of reactants.

Another important task is correlating the particle sizes and shapes with their spectra by using TEM or AFM images.
5.2.2 Silver Nanoparticles

The synthesis of silver nanoparticles described in Chapter 3 is now being used as a method for the synthesis of 10-12 nm silver NPs [1]. The silver NPs can also be used as seeds for the production of silver nanorods of various aspect ratios.

In addition, the 10-12 nm NPs will be used to prepare silver monolayers. The silver nanoparticles can be adsorbed onto pretreated (silanized) glass slides where they “self-assemble” to produce a monolayer. By immersing slides in silver sol and removing them at timed intervals the rate of monolayer formation can be followed by measuring the absorption maximum of each sample.

A surface Beer’s Law constant can be determined for the silver monolayer. The surface coverage of gold nanoparticles can be determined by using the surface analog to the Beer’s Law equation.

\[
A_{\text{surface}} = \frac{\Gamma \varepsilon_{\text{surface}}}{6.02 \times 10^{20}}
\]

\(A_{\text{surface}}\) is the absorbance of surface confined particles. \(A_{\text{surface}}\) is 1/2 the measured \(A\), since only half the surface bound particles are on each side of the glass. \(\varepsilon_{\text{surface}}\) is the surface extinction coefficient at the peak (around 400 nm) for 10-12-nm nanoparticles of silver. \(\Gamma\) is the colloid coverage in number of particles/ cm\(^2\).
References

Appendix A

The Laboratory Experiment: Synthesis and Study of Colloidal Silver
Synthesis and Study of Colloidal Silver

**Purpose:** Colloidal silver is synthesized and its visible spectrum used to find the size of the silver nanoparticles. Aggregation upon addition of salt is observed. A polymer is added to stabilize the colloidal silver.

**Background:**

Nanotechnology deals with processes that take place on the nanometer scale, that is, from approximately 1 to 100 nm. Properties of metal nanoparticles are different from those of bulk materials made from the same atoms. For example, silver metal is grayish, but colloidal silver from this synthesis is a clear yellow. The striking effect of nanoparticles on color has been known since antiquity when tiny metal particles were used to color glass in church windows. Silver particles stained the glass yellow, while gold particles were used to produce ruby glass.

*Synthesis of Colloidal Ag*

Colloidal silver is made by adding an excess of the reducing agent sodium borohydride, NaBH₄ to silver nitrate, AgNO₃.

\[
\text{AgNO}_3 + \text{NaBH}_4 \rightarrow \text{Ag} + \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{B}_2\text{H}_6 + \text{NaNO}_3
\]

The method used in the procedure for this experiment produces nanoparticles that are about 10-14 nm in diameter. The transmission electron microscope (TEM) image shown corresponds to a sample of silver nanoparticles with diameters that are 12± 2 nm. (The length bar is 20 nm.) Particle size can also be determined using visible spectroscopy.

*Spectroscopy and Size of Nanoparticles*

For the 12 nm Ag nanoparticles, the maximum wavelength is near 400 nm. In general, as the particles become larger the absorption maximum shifts to longer wavelengths and the peaks broaden. The peak width at half the absorption maximum is PWHM.

<table>
<thead>
<tr>
<th>Particle size nm</th>
<th>(\lambda_{\text{max}}) nm</th>
<th>PWHM nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-14</td>
<td>395-405*</td>
<td>50-70</td>
</tr>
<tr>
<td>35-50</td>
<td>420</td>
<td>100-110</td>
</tr>
<tr>
<td>60-80</td>
<td>438</td>
<td>140-150</td>
</tr>
</tbody>
</table>

* \(\lambda_{\text{max}}\) may vary from sample to sample.*
Aggregation of Ag Nanoparticles
The Ag nanoparticles that form are stabilized by a protective layer of borohydride ions. Salts such as NaCl or KI shield the negative charges allowing the particles to clump together to form aggregates. To prevent aggregation the nanoparticles can be coated with a polymer such as polyvinyl pyrrolidone (PVP). The structures of the monomer, vinylpyrrolidone, the monomer and the repeat unit of PVP are shown below:

![Vinylpyrrolidone and PVP repeat unit]

PVP inhibits aggregation and stabilizes the colloidal silver even when salt is added.

Apparatus: You will be taking a spectrum of the colloidal silver sol. (Colloidal dispersions of insoluble materials (e.g. silver nanoparticles) are called sols). Refer to the operating instructions. If you are using a Spectronic-20, record %T (easier to read) and convert to A.

Safety and Waste Disposal: Safety glasses are always required in the laboratory. Gloves must be worn throughout this experiment. Silver nitrate is caustic and stains the skin. A container will be made available for any waste solutions.

Procedure:
Glassware was cleaned by soaking in an alcoholic KOH bath, and is ready to use.

Part A: Synthesis of Colloidal Silver
1. Two solutions will be available. 0.0010 M AgNO₃(aq) and 0.0020 M NaBH₄ (aq)

2. Using a graduated cylinder, pour 30 mL 0.0020 M sodium borohydride into the 250 mL Erlenmeyer. Place the Erlenmeyer into an ice bath. Allow to cool for about 20 minutes.

Note: The borohydride solution must be freshly prepared.

3. Place a stir bar in the Erlenmeyer, center the assembly on the stir plate and begin the stirring.
4. Pour 10 mL 0.0010 M AgNO₃ in a buret supported with a clamp and a ring stand. Add the solution dropwise, about 1 drop/second, until it is all used up. This should take around 3 minutes. After 2 mL has been added, the solution should turn light yellow. When all of the silver nitrate has been added, the solution should be a darker yellow.

5. Stop the stirring as soon as all of the silver nitrate solution is added and remove the stir bar.

CAUTION: If the stirring is continued once all the silver nitrate has been added, aggregation is likely to occur; the yellow darkens, turns violet, then grayish as the particles settle out.

6. The product should be clear yellow once the reaction is completed and should remain yellow, although it may darken somewhat. Record the appearance of your product as soon as the stirring is stopped and after waiting for about 5 minutes.

Note: Clear yellow colloidal silver will keep for weeks, even months, when stored in a transparent vial.

Part B: Taking the Spectrum of Colloidal Silver
1. The peak absorbance near 400 nm should be somewhere between 0.5 and 1. Dilute the product with distilled water as needed.

Note: If your product has aggregated and turned gray—repeat the synthesis if possible. Otherwise, a sample will be provided for you to complete parts B and C.

2. Measure the % transmittance (Spectronic-20) every 10 nm between 350 nm and 650 nm, except near 400 nm, where you should record %T every 5 nm.

Note: Pour the diluted colloidal Ag solution into the marked waste bottle.

3. Convert % transmittance to absorbance. Make a plot of absorbance vs. wavelength, by drawing a smooth curve through the points.

4. Record the wavelength of the peak absorbance, $\lambda_{\text{max}}$, and the peak width at half max (PWHM). Compare with tabulated values.

Part C: Aggregation and Stabilization of Colloidal Ag
1. Pour about 2 mL of the clear yellow (undiluted) product into a clean test tube. Add 1 drop of 1.5M NaCl and record any changes.

2. Repeat Step 1 using another clean test tube. Before adding the salt, first add 1 drop of 0.3% polyvinyl pyrrolidone solution. Then, add 1 drop of 1.5M NaCl and record any changes in color. The solution should remain yellow and stable.
3. To find the minimum concentration of PVP needed to stabilize the sol:
Prepare a dilution of the 0.3% PVP and repeat Step 2 until aggregation is observed and you can see a color change. A graduated cylinder can be used for dilutions

Note: The dilution required may be as much as 10 to 1 before the PVP fails to stabilize the colloidal silver.
Data and Results (Colloidal Ag)
Name(s) _________________________________________      Date ________

Part A: Synthesis of Colloidal Silver
Record appearance of your product.

Part B: Taking the Spectrum of Colloidal Silver
1. Dilution required: ________________

<table>
<thead>
<tr>
<th>Colloidal silver solution</th>
<th>Colloidal silver solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_{\text{max}} ) nm</td>
<td>%T</td>
</tr>
<tr>
<td>350</td>
<td>460</td>
</tr>
<tr>
<td>355</td>
<td>470</td>
</tr>
<tr>
<td>360</td>
<td>480</td>
</tr>
<tr>
<td>365</td>
<td>490</td>
</tr>
<tr>
<td>370</td>
<td>500</td>
</tr>
<tr>
<td>375</td>
<td>510</td>
</tr>
<tr>
<td>380</td>
<td>520</td>
</tr>
<tr>
<td>385</td>
<td>530</td>
</tr>
<tr>
<td>390</td>
<td>540</td>
</tr>
<tr>
<td>395</td>
<td>550</td>
</tr>
<tr>
<td>400</td>
<td>560</td>
</tr>
<tr>
<td>405</td>
<td>570</td>
</tr>
<tr>
<td>410</td>
<td>580</td>
</tr>
<tr>
<td>415</td>
<td>590</td>
</tr>
<tr>
<td>420</td>
<td>600</td>
</tr>
<tr>
<td>425</td>
<td>610</td>
</tr>
<tr>
<td>430</td>
<td>620</td>
</tr>
<tr>
<td>440</td>
<td>630</td>
</tr>
<tr>
<td>450</td>
<td>640</td>
</tr>
</tbody>
</table>

\( \lambda_{\text{max}} \) _________ nm \hspace{1cm} \text{PWHM} \hspace{1cm} _________ nm

From the spectrum of your colloidal silver solution, comment on the size of the Ag nanoparticles from your synthesis.
Part C: Aggregation and Stabilization of Colloidal Ag

<table>
<thead>
<tr>
<th>PVP conc Mass %</th>
<th>Color upon addition of 1.5 M NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
</tr>
<tr>
<td>0.3%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Minimum stabilizing concentration of PVP: ________ %

Questions
1. Write the half reaction for the reduction of Ag⁺. Show that NaBH₄ is the reducing agent.

2. Estimate the number of silver atoms in a 12-nm Ag nanoparticle. Assume that each silver atom occupies the volume of a cube with an edge of 0.3 nm. (Volume of a sphere = 4/3 \( \pi \) \( r^3 \))

3. Assuming that the entire silver ion is reduced estimate the number of 12-nm silver nanoparticles produced in your synthesis.

4. Which reactant, silver nitrate or sodium borohydride, is in excess? Give a reason for this. Find the relative number of moles of excess reactant to limiting reactant.
**Instructor Notes**

*Synthesis and Study of Colloidal Ag*

**Time:** 1.5 to 2 h (2 h if the synthesis needs to be repeated)

**Equipment and Materials** (assuming that students work in groups of 2)

<table>
<thead>
<tr>
<th>Items</th>
<th>per group</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>250-mL Erlenmeyer</td>
<td>1</td>
<td>Reaction vessel (precleaned)</td>
</tr>
<tr>
<td>Buret, clamp ,ring stand</td>
<td>1</td>
<td>For adding silver nitrate</td>
</tr>
<tr>
<td>50-mL graduate</td>
<td>2</td>
<td>To measure 30-mL borohydride solution and prepare dilutions of product and PVP</td>
</tr>
<tr>
<td>Stir plate/bar</td>
<td>1</td>
<td>Heating will not be needed.</td>
</tr>
<tr>
<td>0.0010 M AgNO₃(aq)</td>
<td>10 mL</td>
<td>For one synthesis reaction</td>
</tr>
<tr>
<td>0.0020 M NaBH₄ (aq)</td>
<td>30 mL</td>
<td>For one synthesis reaction</td>
</tr>
<tr>
<td>Ice</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test tubes/rack</td>
<td>6 tubes /1 rack</td>
<td>to study aggregation</td>
</tr>
<tr>
<td>Spectronic-20</td>
<td>1 *</td>
<td>* if there are not enough spectrophotometers, groups can share; one group can work on aggregation while the other takes a spectrum</td>
</tr>
<tr>
<td>Cuvettes</td>
<td>2</td>
<td>1 for sample and 1 for blank</td>
</tr>
<tr>
<td>Pasteur pipets</td>
<td>4</td>
<td>For adding PVP, NaCl solutions</td>
</tr>
<tr>
<td>0.3% PVP (aq)</td>
<td>100 mL/class</td>
<td>For the entire class (more than enough)</td>
</tr>
<tr>
<td>1.5 M NaCl (aq)</td>
<td>100 mL/class</td>
<td>For the entire class (more than enough)</td>
</tr>
</tbody>
</table>

**CAS Registry Numbers**

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>CAS Numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium borohydride</td>
<td>16940-66-2</td>
</tr>
<tr>
<td>silver nitrate</td>
<td>7761-88-8</td>
</tr>
<tr>
<td>polyvinyl pyrrolidone</td>
<td>9003-39-8</td>
</tr>
<tr>
<td>potassium hydroxide</td>
<td>1310-58-3</td>
</tr>
<tr>
<td>Ethanol</td>
<td>64-17-5</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>7647-14-5</td>
</tr>
</tbody>
</table>

*All solutions will be provided.*

0.0010 M AgNO₃: Add 0.170 g AgNO₃ to a 1-L volumetric and dilute to the mark with distilled water. (Molar mass of AgNO₃ is 170).

0.0020 M NaBH₄ (aq): Add 0.0378 g sodium borohydride* to a 500 mL volumetric and dilute to the mark with distilled water. (Molar mass of NaBH₄ is 37.8).
0.3% PVP (M = 10,000)
* Occasionally the purity of “99% sodium borohydride” could be lower for particular batch #. Using a newly purchased bottle of sodium borohydride, we found that every attempt to repeat the synthesis failed and resulted in aggregated product. When we contacted Aldrich we were informed that the purity of that particular batch was only 98.39, compared to all other batches that we used which were 98.9%. Instead, you can use the somewhat more expensive 99.995% sodium borohydride.

To purchase from Aldrich:
48,088-6 sodium borohydride granules 99.995% 25 g $45
21,346-2 sodium borohydride 99% 25 g $27

Cleaning Glassware
Alcoholic KOH bath: 1 L 95% ethanol + 120 mL water + 120 g KOH.
Note: The possibility of aggregation increases if the glassware is not thoroughly clean

Typical Results:
Part B: Taking the Spectrum of Colloidal Silver

Spectrum:

\[ \lambda_{\text{max}} = 397 \text{ nm} \]
\[ \text{PWHM} = 70 \text{ nm} \]

Part C: Aggregation of colloidal silver

<table>
<thead>
<tr>
<th>Samples</th>
<th>Conc PVP mass %</th>
<th>Color upon addition of 1.5 M NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Unprotected</td>
<td>0</td>
<td><em>Aggregates: Turns dark yellow, violet, then eventually grayish</em></td>
</tr>
<tr>
<td>2 -?</td>
<td>0.3 to 0.1+</td>
<td><em>Stays yellow</em></td>
</tr>
<tr>
<td>Final</td>
<td>&lt; 0.1</td>
<td><em>Aggregates</em></td>
</tr>
</tbody>
</table>
**Answers to Questions**

1. Write the half reaction for the reduction of Ag⁺. Show that NaBH₄ is the reducing agent.

\[
\text{AgNO}_3 + \text{NaBH}_4 \rightarrow \text{Ag} + \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{B}_2\text{H}_6 + \text{NaNO}_3
\]

\[
\text{Ag}^+ + 1\ e^- \rightarrow \text{Ag}^0 \quad \text{BH}_4^- - 1\ e^- \rightarrow \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{B}_2\text{H}_6
\]

2. Estimate the number of silver atoms in a 12-nm Ag nanoparticle. Assume that each silver atom occupies the volume of a cube with an edge of 0.3 nm. (Volume of a sphere = \(4/3 \pi r^3\))

Volume spherical nanoparticle = \(4/3 \pi 63\) nm³; Volume of a gold atom is about 0.3 nm³

Number of atoms = \(\frac{4/3 \pi 63\text{ nm}^3}{0.3\text{ nm}^3}\) = 33,000 or about 30,000 to 35,000 atoms

(Note: The diameter of a gold atom is 0.288 nm)

3. Assuming that all the silver ion is reduced estimate the number of 12-nm silver nanoparticles produced in your synthesis.

No. Ag NP’s = \(0.0010\ \text{mol Ag}^+ \times \frac{0.010\ L}{1\ L} \times \frac{6.0 \times 10^{23}\ \text{Ag}^+}{1\ \text{mol Ag}^+} \times \frac{1\ \text{Ag}^0}{1\ \text{Ag}^+} \times \frac{1\ \text{Ag NP}}{3.3 \times 10^4\ \text{Ag}^0}\)

\[2 \times 10^{14}\ \text{Ag NPs}\]

4. Which reactant, silver nitrate or sodium borohydride, is in excess? Give a reason for this. Find the relative number of moles of excess to limiting reactant.

\[
\text{AgNO}_3 + \text{NaBH}_4 \rightarrow \text{Ag} + \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{B}_2\text{H}_6 + \text{NaNO}_3
\]

2.0 mmol NaBH₄/L x 0.030 L = 0.060 mmol NaBH₄
1.0 mmol AgNO₃/L x 0.010 L = 0.010 mmol AgNO₃

Sodium borohydride is in excess. This is needed to stabilize the Ag nanoparticles. There is a 6-fold excess of sodium borohydride.
Appendix B

The Laboratory Experiment: Synthesis of Copper Nanoparticles
Prelaboratory Exercise

Experiment 23
Synthesis of Copper Nanoparticles

Name__________________________________ Date______________
Section______

1. For the length units:
   i. centimeter          ii. Ångstrom           iii. micrometer
   a) Give an example that can be used to illustrate the size of each one (such as an
      object or particle or distance).
   b) Convert each unit to nanometers.

2. Compare a colloid consisting of a solid dispersed in water to a solution of a
   solid dissolved in water. Include properties and particle sizes.

3. Write half-reactions \((M^{+n} \rightarrow M^0)\) for the production of the following metals
   upon reduction of their salts:
   a) silver from AgNO₃   b) copper from CuCl₂   c) gold from AuCl₃

Instructor’s Signature ____________________________________________
Experiment 23  
Synthesis of Copper Nanoparticles  

PURPOSE  
Colloidal copper, containing copper nanoparticles (Cu NPs) suspended in water, will be prepared by reduction of copper sulfate using glucose tablets. Different brands of tablets will be compared.

INTRODUCTION  
The size range and surprising color of noble metal nanoparticles is discussed as well as methods for their synthesis and identification.

Size and Color  
Nanoparticles, which have dimensions between 1 and 100 nm, are compared to other “small” particles in the Figure below where you can see that the bacterium is huge in comparison.

Properties of metal nanoparticles are different from those of bulk materials made from the same atoms. Color is the most striking example. The effect of nanoparticles on color has been known since antiquity when the tiny wine-red gold particles were used to make stained glass church windows. In this experiment you will make copper nanoparticles in an aqueous medium. The color of the product will be different from the reddish brown of the bulk metal or the blue-green of aqueous copper ions.

Synthesis  
Noble metal nanoparticles of gold, silver or copper can all be made by adding an excess of reducing agent to a salt of the metal. In this experiment copper sulfate pentahydrate provides Cu(II) ions. The reducing agent is glucose, C₆H₁₂O₆, which reduces copper ion to elemental copper. The glucose itself is oxidized to produce gluconic acid, C₆H₁₂O₇H, which becomes the gluconate ion, C₆H₁₂O₇⁻, in the presence of the base, NaOH.
The reaction can be summarized by the equation below (the solvent is distilled water):

\[
\text{C}_6\text{H}_{12}\text{O}_6^{\text{glucose}} + \text{OH}^-_{\text{Cu}^{2+/\text{Cu}^0}} \rightarrow \text{C}_6\text{H}_{12}\text{O}_7^{\text{gluconate}}
\]

Adsorption of negative gluconate ions gives growing copper nanoparticles a negative surface charge. The nanoparticles are kept suspended in water separated from one another by repulsive electrostatic forces.

**Glucose Tablets**

Glucose tablets, taken to raise low blood sugar, contain ingredients in addition to glucose (Table 23.1) listed on the label in order from most to least. The identity of the ingredients depends on the brand of tablet.

<table>
<thead>
<tr>
<th>Ingredients in Glucose Tablets</th>
<th>Formula</th>
<th>Solubility in H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascorbic Acid</td>
<td>C₆H₈O₆</td>
<td>soluble</td>
</tr>
<tr>
<td>Carageenan</td>
<td>a polysaccharide</td>
<td>soluble</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>C₆H₈O₇</td>
<td>soluble</td>
</tr>
<tr>
<td>Maltodextrin</td>
<td>(C₁₂H₂₀O₁₀)ₙ</td>
<td>soluble</td>
</tr>
<tr>
<td>Xylitol</td>
<td>C₅H₁₂O₅</td>
<td>soluble</td>
</tr>
<tr>
<td>Yellow No. 6</td>
<td>C₁₆H₁₂N₂O₇S₂2Na</td>
<td>soluble</td>
</tr>
<tr>
<td>Cellulose</td>
<td>(C₁₀H₁₀O₅)ₙ</td>
<td>insoluble</td>
</tr>
<tr>
<td>Magnesium Stearate</td>
<td>C₃₀H₇₀MgO₄</td>
<td>insoluble</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>C₁₈H₃₆O₂</td>
<td>insoluble</td>
</tr>
</tbody>
</table>

**Identifying Copper Nanoparticles (Cu NPs)**

Nanoparticles are too small to be observed with an optical microscope. The image on the right was obtained with an electron microscope. The copper nanoparticles shown have diameters that are 18± 2 nm. (The length bar is 20 nm.) A 20-nm spherical particle contains about 150,000 Cu atoms. The appearance of color in the reaction mixture will be used to confirm the presence of Cu NPs.
APPARATUS
Simple equipment including glassware and a hotplate is all that is needed for preparing colloidal copper nanoparticles suspended in water. In fact, this method for the synthesis of metal nanoparticles has been called “metallurgy in a beaker.”

SAFETY
Wear safety glasses and gloves throughout this experiment. Copper sulfate stains the skin.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Toxicity</th>
<th>Flammability</th>
<th>Exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1 M NaOH</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>0.010 M CuSO₄·5H₂O</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

0 is low hazard, 3 is high hazard

PROCEDURE
Choose B.D. (Becton, Dickinson and Company) glucose tablets for Part A of this experiment. Enter the ingredients in the same order in which they appear on the label using the table in the Data/Results page.

Part A: Synthesis of Colloidal Copper

1. Calibrate a disposable pipet. Tare a small beaker, add 40 drops of water, and find the volume per drop (assuming the density of water is 1.0 g/mL).

2. Place 0.80 g glucose tablet in a 50-mL beaker. Using a graduated cylinder, add 10 mL distilled water. With a clean spatula, break up the tablet which should disintegrate and dissolve readily. Filter by gravity into another 50-mL beaker to remove insoluble substances such as magnesium stearate used to make the tablets.

3. Add two drops 1 M NaOH from a disposable pipet.

4. Heat to 50°C on a hotplate. Determine the temperature by immersing a thermometer in a second 50-mL beaker containing water. The thermometer should not touch the bottom of the beaker.

5. Add 0.20 mL 0.010 M CuSO₄·5H₂O by counting drops using the calibrated disposable pipet. Heat until a yellow color appears. Remove from heat. Record the time required for color to appear.

6. Cool to room temperature. Describe the product. Observe any changes in appearance with time.
Part B: Substituting Other Brands of Glucose Tablets

1. Choose another brand of glucose tablet other than the B. D. tablets used in Part A.
   Record the ingredients in the order in which they appear on the label.

2. Repeat the synthesis from Part A and record results.

3. Combining your result with those of other groups complete the table for all of the brands tested in Section B.

4. Which ingredient or ingredients could be inhibiting the reaction?
Data and Results (Copper Nanoparticles)

Name__________________________________ Date______________
Section_____

Part A: Synthesis of Colloidal Copper Using B.D. Glucose Tablets

Describe the reaction including the appearance of the product.

Part B: Synthesis of Colloidal Copper Using Other Glucose Tablets

<table>
<thead>
<tr>
<th>Brand of Glucose Tablet</th>
<th>Ingredients (in the same order in which they are listed on the label)</th>
<th>Result of Reaction with Cu(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.D.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Instructor’s Signature ____________________________________________
Questions

1. For the reaction used in this experiment, give the half reaction for the reduction of ionic copper, and show that copper ion is the oxidizing agent.

2. Which reactant, copper sulfate pentahydrate or glucose, is in excess (the reaction stoichiometry is one mol glucose to one mol copper salt)? How does the excess reactant stabilize the copper nanoparticles?

3. Show that the number of copper atoms in a 20-nm copper nanoparticle is about 150,000. Assume that each copper atom occupies the volume of a cube with an edge of 0.3 nm. (Volume of a sphere = \(\frac{4}{3}\pi r^3\))

4. Which brands (or brand) of glucose tablets produced a color change during the reaction? Which did not? From examining results contributed by the entire class, determine what ingredient or ingredients could be responsible for this. Give your reasoning.
Experiment 23 (Instructor Notes)
Synthesis of Copper Nanoparticles

Time: 2 hours

Equipment and Materials: (class of 20 students with 10 pairs)

<table>
<thead>
<tr>
<th>Items</th>
<th>Am’t/Group</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stir plate/bar</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Disposable pipet</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50-mL beaker</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 M NaOH</td>
<td>1 mL</td>
<td>4 g per liter solution</td>
</tr>
<tr>
<td>Glucose tablets</td>
<td>1</td>
<td>one 4 g tablet/5 rxns; BD and a brand with more citric acid</td>
</tr>
<tr>
<td>0.010 M CuSO₄·5H₂O</td>
<td>1-2 mL</td>
<td>2.50 g CuSO₄·5H₂O per liter sol’n</td>
</tr>
<tr>
<td>Ethanol/KOH bath</td>
<td></td>
<td>cleaning glassware (See Ideas/Info #3)</td>
</tr>
</tbody>
</table>

Ideas/ Information

1. Distilled water must be used in this experiment.

2. Molar masses (g/mol)
   CuSO₄·5H₂O 250
   C₆H₈O₇ citric acid 182
   NaOH 40; C₆H₁₂O₆ glucose (dextrose) 180

3. Cleaning Glassware
   Alcoholic KOH bath: 1 L 95% ethanol + 120 mL water + 120 g KOH.
   The possibility of aggregation increases if the glassware is not thoroughly clean.
   Providing students with clean glassware is recommended.

4. Ingredients in various brands of glucose tablets in the order listed on the label.
<table>
<thead>
<tr>
<th>Orange Glucose Tablets</th>
<th>Ingredients as Listed on the Labels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Walgreens</td>
<td>Dextrose, Cellulose, Maltodextrin, Citric Acid, Magnesium Stearate, Orange Flavor, Ascorbic Acid, Yellow No. 6 Lake</td>
</tr>
<tr>
<td>Dex</td>
<td>Dextrose, Cellulose, Maltodextrin, Citric Acid, Magnesium Stearate, Orange Flavor, Ascorbic Acid, Yellow No. 6 Lake</td>
</tr>
<tr>
<td>BD</td>
<td>Dextrose (glucose), Xylitol, Carageenan, Stearic Acid, Magnesium Stearate, Natural &amp; Artificial Flavors, No Preservatives, Citric Acid</td>
</tr>
<tr>
<td>Rite-Aid</td>
<td>Dextrose (Glucose), Citric Acid, Orange Flavor, Magnesium Stearate, Ascorbic Acid, Color (FD&amp;C Yellow 6), Stearic Acid</td>
</tr>
</tbody>
</table>

5. To test the idea that citric acid inhibits the formation of Cu NPs, citric acid was added to a reaction mixture using pure reagent glucose. There was no color change. In the presence of too much citric acid (an antioxidant) it is possible that the Cu(II) is depleted. BD brand glucose tablets are likely to contain much less citric acid than Dex tablets since citric acid is the last ingredient listed for BD tablets and the 4th for Dex. (see Table in #4 above)
Answers to PreLab Questions

1. For the length units:
   i. centimeter           ii. Ångstrom          iii. micrometer
   a) Give an example that can be used to illustrate the size of each one (such as an object or particle or distance)
   b) Convert each unit to nanometers.

   a) i  diameter of a cuvet used in spectrometers such as the Spec-20
      ii  roughly, the distance between atoms in a chemical bond
      iii  size of a plant cell

   b) i  1 cm x 1 m/10^2 cm x 10^9 nm/m = 10^7 nm
     ii  1 Å x 1 m/10^{10} Å x 10^9 nm/m = 10^{-1} nm
     ii  1 μm x 1 m/10^6 μm x 10^9 nm/m = 10^3 nm

2. Compare a colloid consisting of a solid dispersed in water to a solution of a solid dissolved in water. Include properties and particle sizes.

   Solutions contain particles ranging in size from 0.1 to 10 nm. In colloids the particle size ranges from about 10 to 100 nm. Both solutions and colloids are able to pass through ordinary filter paper.

   In other ways the properties of colloids and true solutions are different, largely because of the size of the colloidal particles. Liquid solutions are transparent, while liquid colloids may be cloudy, because the particles in colloids are large enough to scatter light that is passing through. The scattering, or displacement, of light beams by colloids is called the Tyndall effect. Because colloids deflect light, a beam of light passed through a colloid and viewed at an angle is clearly visible. The same beam of light passed through a solution is not deflected, and when viewed at an angle is only weakly visible.

3. Write half-reactions \( M^{+n} \rightarrow M^0 \) for the production of the following metals upon reduction of their salts:
   a) silver from AgNO₃    b) copper from CuCl₂    c) gold from AuCl₃
   a) \( \text{Ag}^+ + 1 \text{e}^- \rightarrow \text{Ag}^0 \)
   b) \( \text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}^0 \)
   c) \( \text{Au}^{3+} + 3 \text{e}^- \rightarrow \text{Au}^0 \)
Typical Results

Part A: Synthesis of Colloidal Copper Using B.D. Glucose Tablets

Describe the reaction including the appearance of the product.

Within a minute or two the reaction mixture turns light yellow then a darker yellow.
### Part B: Synthesis of Colloidal Copper Using Other Glucose Tablets

<table>
<thead>
<tr>
<th>Brand of Glucose Tablet</th>
<th>Ingredients (in the same order in which they are listed on the label)</th>
<th>Result of Reaction with Cu(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.D.</td>
<td>Dextrose (glucose), Xylitol, Carageenan, Stearic Acid, Magnesium Stearate, Natural &amp; Artificial Flavors, No Preservatives, <strong>Citric Acid</strong></td>
<td>Yellow within 1 min</td>
</tr>
<tr>
<td>Dex</td>
<td>Dextrose, Cellulose, Maltodextrin, <strong>Citric Acid</strong>, Magnesium Stearate, Orange Flavor, Ascorbic Acid, Yellow No. 6 Lake</td>
<td>No color appears</td>
</tr>
<tr>
<td>Rite-Aid</td>
<td>Dextrose (Glucose), <strong>Citric Acid</strong>, Orange Flavor, Magnesium Stearate, Ascorbic Acid, Color (FD&amp;C Yellow 6), Stearic Acid</td>
<td>Bright orange color from added dye makes it impossible to tell</td>
</tr>
</tbody>
</table>
Answers to Questions

1. For the reaction used in this experiment, give the half reaction for the reduction of ionic copper, and show that copper ion is the oxidizing agent.

\[ \text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}^0 \]

Cu\(^{2+}\) gains electrons and thus is the oxidizing agent.

2. Which reactant, copper sulfate pentahydrate or glucose, is in excess (the reaction stoichiometry is one mol glucose to one mol copper salt)? How does the excess reactant stabilize the copper nanoparticles?

mol glucose: \(0.8 \text{ g} \times \frac{1 \text{ mol}}{180 \text{ g}} = 4.4 \times 10^{-3} \text{ mol}\)

mol Cu(II): \(0.00020 \text{ L} \times \frac{0.010 \text{ mol Cu(II)}}{\text{L}} = 2.0 \times 10^{-6} \text{ mol}\)

Glucose is in excess. The gluconate ion that forms in alkaline solution is adsorbed by the Cu nanoparticles giving them a negative surface charge. The Cu NPs are separated by repulsive forces.

3. Show that the number of copper atoms in a 20-nm copper nanoparticle is about 150,000. Assume that each copper atom occupies the volume of a cube with an edge of 0.3 nm. (Volume of a sphere = \(\frac{4}{3} \pi r^3\))

\[
\text{No. Atoms} = \frac{4}{3} \pi \times 10^3 \text{ nm}^3 \div 0.3^3 \text{ nm}^3 \approx 150,000
\]

4. Which brands (or brand) of glucose tablets produced a color change during the reaction? Which did not? From examining results contributed by the entire class, determine what ingredient or ingredients could be responsible for this. Give your reasoning.

BD did, and Dex did not. Citric acid is last on the list of ingredients for BD, but 4th in Dex. Citric acid is an antioxidant and could be interfering with the reaction of Cu(II) with glucose.
References


Vita

Mozhgan Bahadory received her B.S. and M.S. in Chemistry from Azad University, Iran in 1992 and 1996, respectively. In 2002, she earned an M.S. degree in Environmental Engineering from Temple University. Mozhgan enrolled in the Ph.D. program at Drexel University in 2002 and has been working on “The Synthesis of Noble Metal Nanoparticles” under the supervision of Dr. Sally Solomon. She has presented her research at several meetings including the Mid-Atlantic Regional Meeting of the ACS in 2005 and 2006. Mozhgan received a travel award from Eli Lily & Company to present her talk entitled, “Creating Materials for Introducing Nanotechnology into the Chemistry Curriculum,” at the 2007 ACS National Meeting, in Chicago, IL. In 2006, she was awarded the Teaching Excellence Award for her teaching duties as a teaching assistant from Drexel University.

Selected publications from her past and current research:


Solomon, S., Bahadory, M., Rutkowski, S., and Boritz, C., “Extraction of Curcumin from Turmeric”, submitted to Journal of Chemical Education. Replied to reviewers’ comments and resubmitted