Making Nano Gold

Center for Nanotechnology Education

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Making Nano Gold
(Gold Nanoparticle Synthesis)

Abstract

A nanoparticle is defined as a particle between one and about one hundred nanometers (nm) in diameter. At the lower end of this size range, a nanoparticle consists of only a small number of atoms. There is a large variety of nanoparticles, both artificial and naturally occurring, and they can be produced via a large number of methods. In this module students make gold nanoparticles through a chemical process, and examine their optical properties

Outcomes

After completing this module, students will have gained a basic understanding of

- how nanoparticles can be formed in a chemical reaction (oxidation-reduction)
- how the properties of materials may change as their physical size approaches the nanometer scale

Prerequisites

- 8th grade science
- Knowledge of the visible spectrum
- Introduction to ions and their properties

Science Concepts

- Oxidation-reduction reactions
- Electromagnetic nature of light
- Absorption and reflection of different wavelengths of light by materials
- Electrostatic charge and repulsion-attraction of charged bodies

Nanoscience Concepts

- Nanoparticles can be made via “top-down” or a “bottom-up” processes.
- Gold nanoparticles can be produced via a reaction of chemical precursors.
- The properties of a material can dramatically change as the size of a particle approaches the nanoscale.
- As gold particles approach the nanometer scale, they exhibit a marked change in visible color, due to the effect of surface plasmon resonance.

Background Information

Nanoparticles

A nanoparticle is defined as a particle between one and about one hundred nanometers (nm) in diameter. Nanoparticles can be found in several forms, for which different terms are applied. For example, solid nanoparticles suspended in a liquid are called a *dispersion* or a *colloid*, while solid or liquid nanoparticles suspended in air comprise an *aerosol.* Nanoparticles are found throughout the natural environment. Recently, scientists and engineers have developed hundreds of artificial nanoparticles that are used in thousands of products. Nanoparticles were first used intentionally in ancient times to make colored glass, although the glass makers had no idea that nanoparticles were involved. The glass was colored by adding naturally occurring metal oxide powders of various sizes into the molten glass to achieve the desired effect.

Nanoparticles are so small that a large fraction of their constituent atoms reside on the particle surface, much more so than with larger particles in the micron or millimeter size range. Since chemical reactions occur first at the exposed atoms on the particle surface, nanoparticles are very chemically reactive. This property makes nanoparticles very interesting and useful for many applications where surface reactivity is important.

Gold Nanoparticle Synthesis

Nanoparticles can be produced either by "top-down" or "bottom-up" methods. In a top-down process, one starts with a macroscopic piece of material and reduces its size by physically crushing, grinding, and milling. Very intensive and energetic grinding is required to get particles to the nanometer size range, so this approach is only rarely used. More commonly, nanoparticles are produced in a bottom-up process, where the particles grow from free molecules or atoms in a chemical process. The gold synthesis described here uses a liquid chemical method involving an oxidation-reduction ("redox") reaction between two precursor chemicals, gold chloride hydrate ($HAuCl_4$, also called hydrogen tetrachloroaurate) and sodium citrate dihydrate.

The reaction begins by dissolving $HAuCl_4$ in water, which releases the Au^{3+} ions into solution. Under rapid stirring, the sodium citrate is added, which acts as a *reducing agent*. A reducing agent is an element or compound that loses an electron to another chemical species in a redox chemical reaction. When a reducing agent loses electrons, it is said to be *oxidized*. In this case, the redox reaction causes the Au^{3+} ions in solution to gain electrons (i.e., be *reduced*), making them neutral gold atoms. After the redox reaction starts, the gold that had been in solution becomes supersaturated--it begins to precipitate out of the solution and form clusters of gold atoms, a process called *nucleation.* As the redox reaction proceeds the newly formed gold atoms stick to these nucleated clusters (*nuclei)*, causing the new nanoparticles to grow in size from 1-3 nm to around 20 to 30 nm. If the solution is stirred vigorously, all the nuclei grow to become fairly uniformly-sized nanoparticles.

The reducing agent in this reaction is sodium citrate, which was first used for gold nanoparticle synthesis by J. Turkevich in 1951; thus this reaction is known as the Turkevich method. If one uses less sodium citrate, larger particles can be produced. Less sodium citrate in the reaction means that fewer stable nuclei form initially. As more gold atoms react and precipitate, they have fewer places to attach, so they stick to these nuclei forming a dispersion of fewer, but larger, nanoparticles.

Gold Nanoparticle Color

A macroscopic chunk of gold, like a gold ring, has a bright light yellow color. On the other hand, the color of gold nanoparticles ranges from cloudy orange to deep red to dark purple, depending on the nanoparticles' mean size. This change in color is due to a process called *surface plasmon resonance*. All metals have many loosely bound free electrons, which determine their electrical and optical properties. When a metal like gold is exposed to light, the oscillating electric fields of the light wave will cause these free electrons to oscillate; these resonant oscillations are known as surface plasmons. Due to plasmon resonance, some wavelengths (i.e., colors) of light will be strongly absorbed by the gold and removed from the light spectrum, while the rest will be unaffected by the metal and will be reflected to our eyes. When bulk gold metal is illuminated with white light, it absorbs energy from the blue-violet end of the spectrum as well as the red-infrared, which leaves the yellow part of the spectrum to be most strongly reflected and giving bulk gold its characteristic color. On the other hand, gold nanoparticles interact with light differently. Surface plasmon resonance causes small, newly formed gold nanoparticles (typically around 20 nm in size) to absorb in the blue-green part of the spectrum and strongly reflect the red wavelengths, giving the dispersion a deep red color. As particle size increases, the wavelength of surface plasmon resonance-related absorption shifts to longer, redder wavelengths. Red light is then absorbed, and blue light is reflected, yielding dispersions with a pale blue or purple color. If the particles become large enough to be comparable to a wavelength of visible light (400-700 nm) they will scatter all wavelengths of white light, giving the dispersion a whitish cloudy appearance.

Keeping Gold Nanoparticle Dispersed

Beside acting as a reducing agent in this reaction, the sodium citrate also provides a molecular coating on the surfaces of the newly created nanoparticles, giving them a negative charge. These like-charged gold nanoparticles strongly repel each other, which prevents further particle clustering and maintains a stable dispersion. Adding more ions to the dispersion, like those from a salt solution, will weaken the particles' repulsion and allow them to cluster into larger size ranges. This is what happens when a salt solution like NaCl is added to the gold nanoparticle dispersion. Evidence of increasing particle size include changing dispersion color and increased dispersion cloudiness. One can get an idea of the presence of larger particles by observing a laser beam traveling through the dispersion. True nanoparticles are too small to scatter much light out to your eyes and are thus not visible, but particles that have grown to be ≥250 nm will scatter the laser light so that it is visible.

Current and Future Applications

A wide variety of different types of nanoparticles are used in products used in foods, inks, paints, pharmaceuticals, coatings, cosmetics, and personal care items. You can find zinc oxide nanoparticles in sunscreen, silver nanoparticles in bandages, silicon nanoparticles in solar cells, and carbon nanotubes in bicycles and sporting equipment. Coatings and materials such as ceramics and composites have nanoparticles in them to color and strengthen the material.

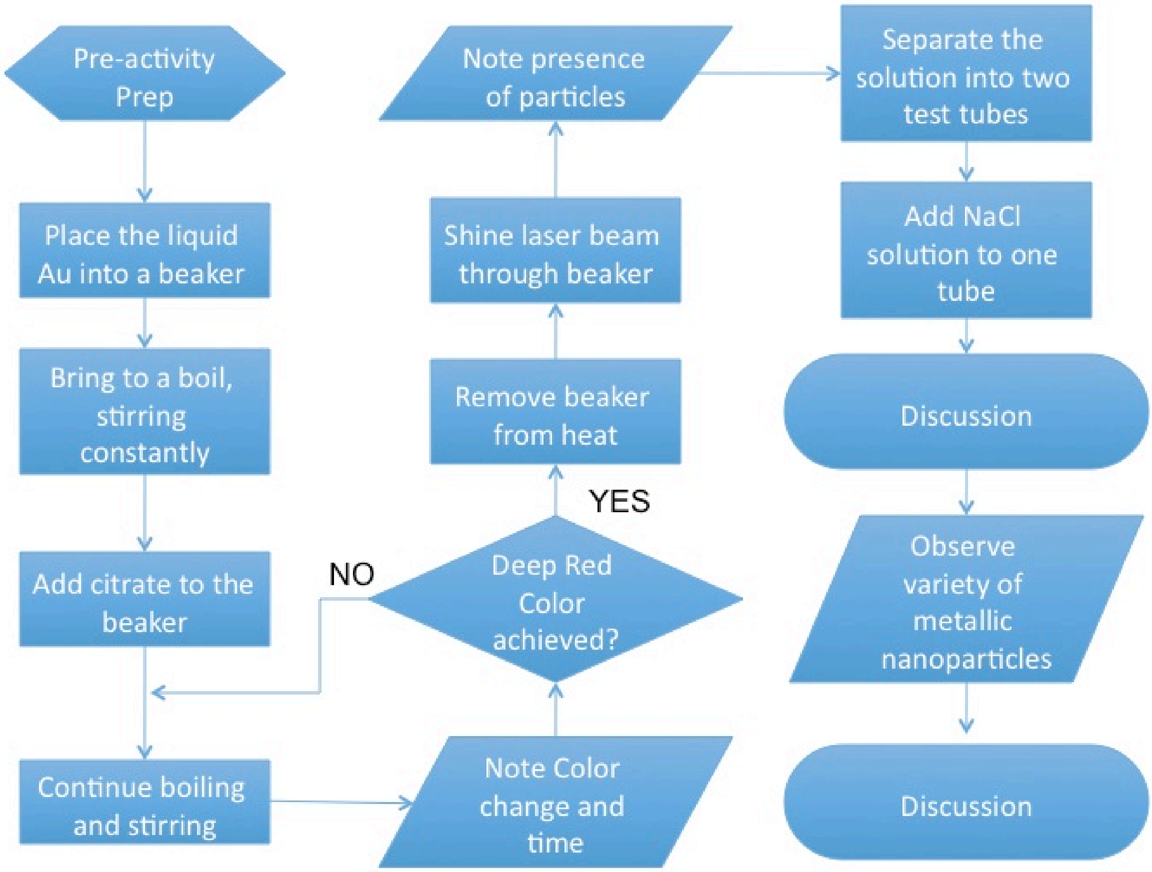
Presently, gold nanoparticles find wide use in medical therapies that attempt to deliver a drug precisely to the place in the body where it is needed. This is useful for drugs like chemotherapy agents for cancer, which present a toxic risk to healthy tissues. In *targeted drug delivery*, molecules of the desired drug are chemically bonded to the surfaces of gold nanoparticles. Also attached to each particle is a protein that allows the particle to "recognize" the targeted tumor by the shape of its surface proteins. By targeting the drug to the cancer in this way, more of the drug is delivered to the tumor, reducing the potential for damage to healthy tissues. Gold is quite biocompatible with living tissues, making it widely used for drug targeting. The use of gold nanoparticles for advanced drug therapies will continue to grow in the future.

Instructor Notes

Safety: Students should wear eye protection and latex or nitrile gloves. Remind them to never look directly into a laser or shine one at another person.

Learning Activity: Making Nano Gold

Activity Flow Chart



Activity: Making Nano Gold

Materials

To make stock solutions for 25 batches:

- 1.0 mM hydrogen tetrachloroaurate: The solid is hygroscopic so purchase $HAuCl_4{\cdot}3H_2O$ (Aldrich 244597 or 520918) in 1.0 g quantities and use the entire bottle. Dissolve 1.0 g HAuCl4.3H2O in 250 mL distilled water to make a 10.0 mM stock solution of gold(III) ions that can be kept for years if stored in a brown bottle. Dilute 25 mL of stock to 250 mL to make the 1.0 mM concentration for this experiment.

- 1% trisodium citrate dihydrate: Dissolve 0.5 g $Na_3C_6H_5O_7{\cdot}2H_2O$ (sodium citrate) in 50 mL distilled water.

- NaCl solution: Dissolve at least 0.5 g of NaCl in 10 mL distilled water or use a saturated solution.

- Optional sports drinks: Gatorade Ice, Powerade, flavorless Pedialyte, pickle juice. Liquids that are colorless or have as little color as possible work better.

- Metal oxide dispersions. Suggested options are zinc oxide and titanium dioxide. These can be purchased from a hobby/ceramics store or from Aldrich.

Equipment and Supplies

- 50 mL Erlenmeyer flask or beaker
- Graduated cylinder
- Short stir bar (~1 cm)
- Stirring hotplate
- Laser pointer, polarizing filter (optional)
- Droppers
- Small test tubes
- Small vials (~20 ml), optionally with a small magnifying lens in the bottom. These can be purchased from hobby/rock hound stores.

Activity Part One

Procedure

Prep: Rinse all glassware with pure water before starting.

1. Add 20 mL of 1.0 mM $HAuCl_4$ to a 50 mL beaker or Erlenmeyer flask on a stirring hot plate.
2. Add a magnetic stir bar and bring the solution to a rolling boil.
3. To the rapidly-stirred boiling solution, quickly add 2 mL of a 1% solution of trisodium citrate dihydrate, $Na_3C_6H_5O_7{\cdot}2H_2O$.

4. Remove from heat when the solution has turned deep red or after 10 minutes have elapsed.
5. Shine a laser pointer through the flask.
    - The presence of particles can be detected by the laser beam light scattered from the particles.
    - The light from a laser pointer may be polarized. When polarized light interacts with nanoparticles, the beam may disappear at some angles. When the beam from the laser is visible, is it invisible in a view perpendicular to the first?
6. Put a small amount of the gold nanoparticle solution in two test tubes.
7. Use one tube as a color reference and add 5-10 drops of NaCl solution to the other tube.
    - Record any change in the nanoparticle dispersion you observe.
8. Test the ionic content in sports drinks by counting the drops needed to change the color of 7 drops of gold nanoparticle dispersion.
    - Record any change in the nanoparticle dispersion you observe
    - Compare this to what you observed using the NaCl solution

Discussion

What did you observe as the gold dispersion formed?

Answer: The gold nanoparticle dispersion gradually forms as the citrate reduces the gold ions to neutral metallic gold.

What did you observe as you added NaCl solution to the gold dispersion?

Answer: The color of the solution changed with the addition of sodium chloride. The addition of these dissolved ions reduces the repulsion of the like-charged gold nanoparticles, which allows the nanoparticles to move closer together. Eventually they begin to agglomerate and get larger, changing their effect on scattered white light (that is, changing the color of the light we see).

How did the effects of adding the NaCl and the various sports drinks compare?

Answers may vary.

Activity Part Two

Procedure

1. Obtain a vial of the suspended metal oxides.
2. Shine a laser through the vial.
3. Observe particles. If a camera is available, take a picture to reveal the particles in the suspension. (There is an example in the slideshow)

Discussion

What did you observe as the laser light passed through the metal oxide dispersion?

Answer: The laser's path through the dispersion was visible, due to the particles scattering light back to our eyes.

Contributors

- This module was written by Billie Copley (Dakota County Technical College, Rosemount MN) and Kim Grady (BehaveHeuristics, LLC, Phoenix AZ), and edited by Jim Marti University of Minnesota, Minneapolis MN).
- The activity in this module is based on "Gold Nanoparticles" from MRSEC Education Group, University of Wisconsin: www.education.mrsec.wisc.edu/nanolab/gold/index.html
- The electrolyte analysis of sports drinks was developed by Andrew Greenburg (University of Wisconsin, Madison WI).

Resources

Videos

http://www.youtube.com/watch?v=urmi99jQSZY

Simulations

http://etlab.eng.uab.edu/gold-nanoparticle-simulation/

Articles

1. The chemistry behind this activity: D. McFarland, C. L. Haynes, C. A. Mirkin, R. P. Van Duyne, and H. A. Godwin, "Color My Nanoworld," J. Chem. Educ. (2004) 81, 544A.
2. An introduction to colloids: https://en.wikipedia.org/wiki/Colloid
3. An explanation of coloring glass with metal and metal oxides: https://en.wikipedia.org/wiki/Glass_coloring_and_color_marking
4. An introduction to plasmon resonance: http://en.wikipedia.org/wiki/Plasmon