Color My Nanoworld

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This Activity introduces students to the unique properties of nanoscale materials through exploration of size-dependent optical properties of gold nanoparticles. Students determine that a gold nanoparticle solution functions as an electrolyte sensor because electrolyte-induced aggregation of the nanoparticles results in a dramatic color change.

Background

In this Activity, students follow the process of nanoparticle aggregation by observing the color change of a solution of gold nanoparticles. Students prepare a solution of well-separated, 13 nm-diameter gold particles. A layer of citrate anions adsorbed to each nanoparticle's surface produces an electrostatic repulsion that keeps the nanoparticles separated. In this state, the solution absorbs 520 nm (green) light strongly and the solution appears red. Instructors might use a color wheel to demonstrate the relationship between the color an object absorbs and the color that it appears. When a strong electrolyte is added to the solution, the high concentration of ions screens the repulsive electrostatic forces between nanoparticles. Because the repulsive force is eliminated, the gold nanoparticles aggregate. As the spacing between the nanoparticles decreases to less than their average diameter, the solution absorbs light at longer wavelengths (650 nm). Accordingly, the solution turns blue. If a larger quantity of the electrolyte is added, large nanoparticle aggregates precipitate and the solution becomes clear. If a non- or weak electrolyte is added, the electrostatic repulsions between the gold/citrate particles are not disrupted. The solution remains red. A diagram of these processes is available on *JCE Online*.[W]

Integrating the Activity into Your Curriculum

This Activity provides an introduction to scientific notation and orders of magnitude by exposing students to nano-sized materials. Challenge the students to identify an object corresponding to each order of magnitude from $1–10^{-10}$ m. Instructors can emphasize that the changes observed in this Activity correspond to physical rather than chemical changes. This Activity provides connections to topics such as electrolytes, complementary colors, and spectroscopy.

About the Activity

Prepare stock solutions in advance. Prepare 1.0 mM $HAuCl_4$ by dissolving 0.1 g of the solid in 500 mL of distilled water. Prepare a 38.8 mM $Na_3C_6H_5O_7$ (sodium citrate) by dissolving 0.5 g of the solid in 50 mL of distilled water.

Hydrogen tetrachloroaurate trihydrate, $HAuCl_4 \cdot 3H_2O$ (#G4022), and sodium citrate dihydrate, $Na_3C_6H_5O_7 \cdot 2H_2O$ (#S4641), are available from Sigma–Aldrich, St. Louis, MO (800/325–3010). 1 g $HAuCl_4 \cdot 3H_2O$ is ~$24. This makes 5 L of stock solution, enough to perform the Activity 250 times. Unused Au nanoparticle solution made in Part A can be stored for several years in a brown bottle. 1.0 mM $HAuCl_4$ stock solution is unstable and will last only a few days.

With a spectrophotometer, students can monitor the nanoparticle aggregation by the UV-visible absorption of the solution. This allows the students to associate the absorbed wavelength (measured from the spectrum) with the observed color of the solution. Advanced experiments have been developed for undergraduate laboratories that investigate the adsorption of the Au nanoparticles to chemically-modified surfaces *(1)*.

Answers to Questions

1. Electrostatic repulsion caused by the adsorbed anionic citrate layer prevents the nanoparticles from aggregating.
2. Electrolytes, like dissolved salt, are able to screen the repulsive electrostatic forces of the citrate layer because the positive charges of the electrolyte associate with the negative charges on the surfaces of the nanoparticles. Non-electrolytes, like dissolved sugar, do not screen the repulsive forces.
3. Interactions between complementary strands of DNA links particles *(2)*. Antibody/antigen pairs also selectively link. By modifying the surfaces of the nanoparticles to incorporate these biomolecules, binding events can be detected by a change in solution color.

References, Additional Related Activities, and Demonstrations

1. Keating, Christine D.; Musick, Michael D.; Keefe, Melinda H.; Natan, Michael J. Kinetics and Thermodynamics of Au Colloid Monolayer Self-Assembly: Undergraduate Experiments in Surface and Nanomaterials Chemistry. *J. Chem. Educ.* **1999**, *76*, 949–955.
2. More information about DNA-directed nanoparticle assembly is at *http://www.chem.northwestern.edu/~mkngrp/BioNanomaterials2003rev1.htm* (accessed Feb 2004)

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One nanometer is 10,000 times smaller than the diameter of a human hair. Can you imagine producing and using nanometer-sized materials? Nanoscience investigates the properties of these materials. By understanding these properties and learning how to utilize them, scientists and engineers can develop new types of sensors and devices. This technology could have a huge impact on diagnosing diseases, processing and storing information, and other areas.

Physical and chemical properties are size-dependent over a certain size range specific to the material and property. When a particle of gold metal is similar in size to wavelengths of visible light (400–750 nm), it interacts with light in interesting ways. The color of a gold nanoparticle solution depends on the size and shape of the nanoparticles. Consider this analogy: tapping a spoon on a glass bottle partly filled with water generates a sound. Vary the volume of water in the bottle and the tone of the sound changes. The tone is dependent on the volume of water. Similarly, the volume and shape of a nanoparticle determines how it interacts with light. Accordingly, this determines the color of a nanoparticle solution. For example, while a large sample of gold, such as in jewelry, appears yellow, a solution of nano-sized particles of gold can appear to be a wide variety of colors, depending on the size of the nanoparticles. In this Activity, you will explore these size-dependent properties of gold nanoparticles and investigate the effect of adding different substances.

Try This

You will need: 1.0 mM $HAuCl_4$ and 38.8 mM $Na_3C_6H_5O_7$ (sodium citrate) solutions from your instructor, 50-mL beaker, magnetic stir bar, stir/hot plate, distilled water, table salt (NaCl), table sugar (sucrose), four glass vials or clear, colorless plastic cups, two small containers, dropper, balance, and graduated cylinder.

Be Safe! Gloves should be worn when working with the nanoparticle solution. Rinse used solutions down the sink. If substances other than salt and sugar are added to the nanoparticle solution, dispose of the nanoparticle solution using methods appropriate for solutions containing those substances.

A. Preparation of 13 nm-Diameter Gold Nanoparticles

__1. Pour 20 mL of 1.0 mM $HAuCl_4$ (from your instructor) into a 50-mL beaker. Add a magnetic stir bar. Heat the solution to boiling on a stir/hot plate while stirring with the magnetic stir bar.

__2. After the solution begins to boil, add 2 mL of 38.8 mM $Na_3C_6H_5O_7$ (from your instructor). Continue to boil and stir the solution until it is a deep red color (about 10 min). As the solution boils, add distilled water as needed to keep the total solution volume near 22 mL. How does the solution visibly change? The sodium citrate reduces the Au ions to nanoparticles of Au metal. Excess citrate anions in solution stick to the Au metal surface, giving an overall negative charge to each Au nanoparticle.

__3. When the solution is a deep red color, turn off the hot plate and stirrer. Cool the solution to room temperature before using it in Part B.

B. Nanoparticles As Chemical Selective Sensors

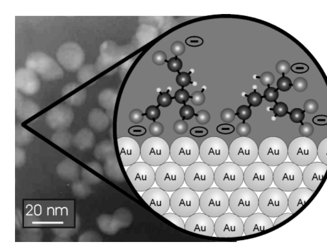
__1. In a small container, dissolve 0.5 g of table salt (NaCl) in 10 mL of distilled water to make a ~1 M solution.

__2. In a small container, dissolve 2 g of table sugar (sucrose) in 10 mL of distilled water to make a ~1 M solution.

__3. Into each of four glass vials or clear, colorless plastic cups, place 3 mL of the gold nanoparticle solution you prepared in Part A. Add 3 mL distilled water to each vial.

__4. With a dropper, add 5–10 drops, one at a time, of the salt solution from part B, step 1 to one of the vials. Record your observations. (Refer to an unused solution for comparison.) What is happening to the nanoparticles in solution?

__5. With a dropper, add 5–10 drops, one at a time, of the sugar solution from part B, step 2 to one of the vials containing fresh nanoparticle solution. Record your observations. (Refer to an unused solution for comparison.)



Left: A micrograph of 13 nm-diameter Au nanoparticles. Right: An illustration an Au nanoparticle surface. Each nanoparticle is made of many (more than 500,000) Au atoms. Citrate anions cover the nanoparticle surface.

__6. Choose another substance to add to a third vial. One suggestion is a household liquid such as vinegar. Check with your instructor about your choice. Before adding the substance, predict whether or not a color change will occur.

Questions

1. Based on the fact that the citrate anions cover the surface of each nanoparticle, explain what keeps the nanoparticles from sticking together (aggregating) in the original solution.
2. Why does adding the salt solution produce a different result from adding the sugar solution?
3. How could the effect in part B be used to detect the binding of biomolecules, such as DNA or antibodies, that stick to one another or to other molecules? How could these molecules be used to cause aggregation of the nanoparticles?

Information from the World Wide Web *(accessed February 2004)*

National nanotechnology initiative: for students K–12. *http://www.nano.gov/html/edu/eduk12.html*