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**The Preparation and Characterization of Nanoparticles (Nano)**

Created by Dr. Grice, based a variety of sources.

Solid-state materials play an increasing role in inorganic chemistry, material science, and biotechnology. In addition to metal surfaces, complex solid-state materials such as metal-organic frameworks (MOFs), nanoparticles, zeolites, and perovskites have various applications such as sensing, energy, medicine, and catalysis. Materials with nanometer-scale geometries generally behave quite differently from standard bulk materials and this type of size-dependent behavior has been exploited for a variety of applications. Unfortunately, we cannot use standard solution-phase techniques such as NMR to analyze these materials, and advanced X-ray analysis and microscopy techniques such as SEM and TEM are beyond the scope of this course. Also, I destroyed the powder XRD with my bare hands when I started here at DePaul (sorry…. well, not really, I needed the space). In this lab, we will be examining the properties of nanoparticles by synthesizing two different types of nanoparticles: magnetic iron nanoparticles, and gold nanoparticles.

 In the first day, you will synthesize iron oxide nanoparticles and suspend them in solution to make a ferrofluid. This ferrofluid exhibits very interesting properties in the presence of a magnetic field (such as those generated by a permanent magnet). The ferrofluid is composed of magnetite (Fe3O4) nanoparticles suspended in solution. Magnetite is a mixed-valence material, with iron in both the +3 and +2 oxidation states.

 In the second and third days, you will synthesize nanoparticles and explore the optical properties of these nanoparticles as a suspension in solution. You can start the gold nanoparticle synthesis on the first day if you have time. Gold nanoparticles are synthesized from the reduction of Au(III) by citrate. Gold nanoparticles have been extensively studied as materials for sensing, due their interesting optical properties. We will synthesize gold nanoparticles, take a UV-Vis spectrum, and then take a UV-Vis spectrum in the presence of an analyte (chloride).

**EXPERIMENTAL PROCEDURE**

*Notes:* This experiment can be performed over 3 laboratory periods.

*Safety:* Metal salts are hazardous. Nanoparticles and solvents are potentially carcinogenic and should be handled with care. Discard all waste in the proper containers.

**Preparation of magnetite nanoparticles:**

 In a 100 or 150 mL beaker, combine 5.0 mL of 1M FeCl3 and 1.0 mL of 2M FeCl2 solution. Stir continuously as you add 50 mL of 1.0 M NH3 *over a period of 5-10 minutes* (add about 1 mL every 10 seconds). **Do not add the solution all at once**. Black particles should begin forming. When you are done adding the ammonia solution, place a magnet under the container and let the solid settle. Decant and discard the clear solution without losing the solid (the solid should respond to the magnet).

Transfer the solid to a plastic weigh boat with the aid of a small amount of water from a wash bottle. Use the magnet to keep the solid at the bottom of the weigh boat and discard the liquid, keeping the solid. Rinse the solid once more with water and decant. Remove the magnet. Add 1-2 mL of 25% tetraethylammonium hydroxide to the residue. Stir with a glass rod for 1-2 minutes. This will begin to form the ferrofluid. Use a strong magnet to attract the ferrofluid to the bottom of the weighing boat. Pour off and discard the dark liquid. Move the magnet around and again pour off any liquid. If the ferrofluid does not spike, continue to move the strong magnet around, pouring off any liquid. Examine the spikes that form as you move the magnet around. Record your observations and take a picture!

**Preparation of gold nanoparticles:**

 Gold nanoparticles are formed by the reduction of soluble gold species. Add 20 mL of a 1.0 mM HAuCl4 to a 50 mL beaker with a stir bar on a stir plate. Stir and heat the sample to a roiling boil. To the rapidly-stirred boiling solution, quickly add 2 mL of a 1% solution of trisodium citrate. The gold sol gradually forms as the citrate reduces the gold(III). Remove the beaker from heat when the solution has turned **deep red**. Shine a laser pointer through the solution and note your observations (the instructor will provide the laser). Record a UV-Vis spectrum of your solution, diluting as needed to get the spectrum on scale. Measure the location of the major peak and also the peak width at half height for the major signal, and other data as necessary (see below). If you need to store your nanoparticles for the next lab period, give a solution to your instructor in a scintillation vial and they will be stored in the freezer.

**Analysis of analytes using gold nanoparticles**

 Put a small amount of the gold nanoparticle solution in two test tubes. Use one tube as a color reference and add 5-10 drops of a NaCl solution to the other tube. Does the color of the solution change as the addition of chloride? In a cuvette, take a UV-Vis of your nanoparticles, then add 0.1 mL of the NaCl solution to the tube. Record the UV-vis spectrum and then repeat, until you have 3 spectra with differing amounts of NaCl added. What changes do you observe?

**REPORT**

Be sure to include the following:

1. Any necessary balanced chemical equations

2. A picture of your ferrofluid in the presence of a magnetic field

3. UV-Vis spectra of your gold nanoparticles as synthesized and in the presence of your analyte.

**PROBLEMS (to be addressed in the intro or discussion of your lab report, as appropriate)**

1. What is the difference between ferromagnetism and paramagnetism?

2. What roles do magnetite and/or magnetic iron oxides play in biology?

3. What are “quantum dots”?

4. Why is the color of gold nanoparticles different than the color of metallic gold?

5. Estimate the size of your nanoparticles by using one of the equations found in Anal. Chem. **2007**, *79*, 4215-4221.

6. Determine the average number of atoms per nanoparticle using the following formula:

N = number of atoms per nanoparticle

π = 3.14159…

ρ = density of face centered cubic (fcc) gold = 19.3 g/cm3

D = average diameter of nanoparticles (from problem #5 above)

M = atomic mass of gold

NA = number of atoms per mole

Note: This assumes that the nanoparticles have a spherical shape and a uniform fcc crystalline structure. Be careful about units.

7. Determine the molar concentration of the nanoparticle solution using the following formula:

C = molar concentration of nanoparticle solution

NT = Total number of gold atoms added as HAuCl4

N = number of atoms per nanoparticle (from calculation #6)

V = volume of the reaction solution in L

NA = number of nanoparticles per mole

Note: This equation assumes that the reduction of Au3+ to Au0 was complete.

8. In theory, could a calibration curve be made to analyze for chloride using gold nanoparticles based on your observations?