

Materials in nanoscale: Size matters

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Summary

Students will prepare aqueous solutions of silver nanocrystals of different sizes using simple redox chemistry. Silver nanocrystals of different particle size will exhibit different optical absorption and plasmon scattering spectrum. Students will measure the absorption spectrum and discuss how such size-dependent properties of nanoscale materials are utilized in the applications.

Concept

Nano materials, Redox reaction, Light absorption, Spectroscopy

Materials provided

1. Chemicals

- 1.25×10^{-2} M of aq. sodium citrate solution in a plastic bottle
- 3.75×10^{-4} M aq. silver nitrate solution in a plastic bottle
- 5.0×10^{-2} M aq. hydrogen peroxide solution in a plastic bottle
- 1.0×10^{-3} M aq. potassium bromide solution in a plastic bottle
- deionized (DI) water
- sodium borohydride in a glass vial (Instructor should see *Notes for instructor* included in the CD rom)

2. Glassware and other apparatus

- glass vials with caps for the synthesis
- water squirt bottle
- plastic cuvettes
- plastic syringes
- micropipette (10-100 μ L) - (Instructor should see *Notes for instructor* included in the CD rom)

3. Equipment

- 3 sets of UV-Vis spectrometers and USB cables

Materials required at school (glassware may be provided per request if not available)

- disposable plastic gloves
- safety glass or goggles
- graduated cylinders (20-30 ml)
- beakers or any container that can hold the sample solutions of 50 ml (four per group)
- printer (optional)

Chemical safety and waste disposal

The chemicals supplied in solution form are relatively harmless. If spilled on skin, wash with tap water. Avoid contact to eyes. See also included MSDS in CD rom. See also the *Notes for instructor*.

Chemical waste disposal

Sodium citrate solution and hydrogen peroxide solutions can be disposed of to the sink with excess water.

Silver nitrate solution and the synthesized silver nanocrystal solution should be collected in a chemical waste bottle.

(Instructor should see *Notes for instructor* included in the CD rom)

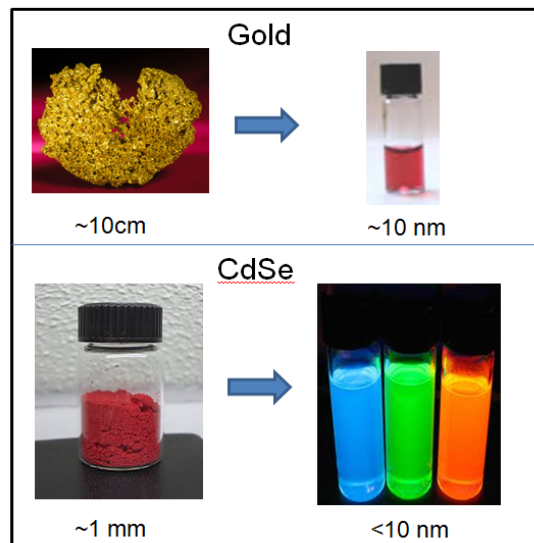
Activity

The activity is composed of two parts. (i) Synthesis of the silver nanoparticles of varying size that show different colors, (ii) measurement of UV-Vis spectrum to characterize their optical absorption to correlate the wavelength of the absorption and the size of the particle. Before doing the experiments, following discussions may be made to learn the general background of nano materials.

1. Why is 'nano' interesting ?

Many materials, such as metals and semiconductors, change their property drastically when their size becomes small in 1-100 nm range. This is because the electrons in these materials determining many of the chemical and physical properties of these materials do not behave in the same way as in the bulk when the size of the material shrinks to nanometer scale. Electrons feel too 'confined' in small space of the nano-sized materials. Examples are localized surface plasmon in metal nanocrystals or quantum confined exciton in semiconductor nanocrystals.

The figure on the right side shows a few examples how varying the size of the materials radically changes their optical properties. Metallic gold is shiny yellow. When the size of the gold is in the range of 10-100 nm and dispersed in water, it shows different color that varies with size. Semiconductor nanocrystals, such as CdSe, also absorb and emit the light at different wavelengths depending on the size of the nanocrystal. In this figure, emission of different color from CdSe nanocrystals under ultraviolet illumination is shown.



<http://archive.fieldmuseum.org>
<http://cnx.org/content/m22374/latest/>

2. Is the peculiar property of 'nano' materials useful?

Because now we can control and tune the material properties of metals and semiconductor simply by changing their size, we can use these nano materials in various applications, where color tunability is required. Metal nanoparticles are particularly strong absorber of light and can be used also as the nano heater heated by light. Some of the applications of nanocrystalline materials list below

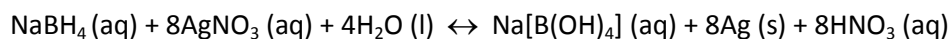
- Luminescent tracers in bio-imaging: semiconductor nanocrystals are very bright and color-tunable, and they can be used to stain the biological tissues, which can be detected with microscope very easily.
- Cancer treatment via hyperthermia: metal nanocrystals that can absorb near infrared light very strongly can be injected into cancer cells. Shining the infrared lamp over the nanocrystal-bearing cancer tissue heats up and kills the cancer cell.
- Many researchers are working on making efficient solar cell or LED devices made of semiconductor nanocrystals

3. Experimental activity

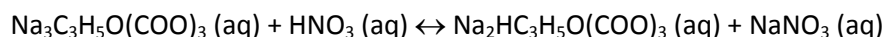
a) Synthesize of silver nanocrystals of different sizes

The synthesis of silver nanoparticles are done using the following reactions. The reactions and procedures are adapted from J. Chem. Edu. (2010), 87, 1098

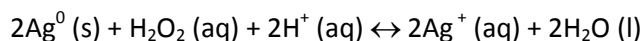
- Sodium borohydride is used to reduce silver nitrate. As the Ag ions are reduced, Ag atoms begin to aggregate, forming a well-defined nanoparticle in the presence of surface-stabilizing agents.



- Excess sodium citrate acts as a buffer to maintain neutral or weakly basic pH of the solution and also act as stabilizer keeping the nanoparticles separated from each other. Without proper stabilization, reduction of silver ions leads either to bulk metal (silver mirror reaction) or black precipitate.



- Hydrogen peroxide facilitates formation of prism shaped nanoparticles by etching.



- KBr is added to the reaction to alter the size at which the particle stops growing. KBr limits the growth of the silver nanoparticles by binding to the silver nanoparticle surface.

1. Each group needs the following solutions in the beakers (or any container).

Label the beakers A to E. You can use graduated cylinder to transfer the solution from the plastic bottle to the beaker. Instructor should see the *Notes for instructor*.



- (A) 20 ml of sodium citrate solution ($\text{Na}_3\text{C}_3\text{H}_5\text{O}(\text{COO})_3$)
- (B) 30 ml of silver nitrate solution (AgNO_3)
- (C) 30 ml of hydrogen peroxide solution (H_2O_2)
- (D) 20 ml of potassium bromide solution (KBr)
- (E) 30 ml sodium borohydride solution (NaBH_4)

2. Label the cap of the provided vials I-IV.



3. In all four vials, add 2 ml of solution (A). Use the plastic syringe to measure the volume and transfer the solution. For step 3,4,5 and 8, a separate syringe should be used to transfer each solution. Each group will need four syringes. It will be convenient to label each syringe A,B, C and E.

4. In all four vials, add 5ml of solution (B) in the same ways as in step 3.
5. In all four vials, add 5ml of solution (C) in the same ways as in step 3.
6. Add 0, 15, 22 and 40 μL of solution (D) respectively to vial (I)-(IV) using the micropipette. This step should be performed by an instructor using the provided micropipette. (Instructor should see the included video clip how to use micropipette.wmv)
7. Place the cap on each vial and mix the solutions well by shaking.
8. Open the cap, and add 2.5ml of solution (E) to all four vials in the same way as in step 3. This step will initiate the reduction reaction and other reactions forming the silver nanoparticles.
9. Replace the cap on the vial and shape the vial. The color will begin to appear and it will change over time. It will take up to several minutes to reach the final color.

b) *UV-Visible absorption spectrum measurement*

Absorption spectrum of the four nanocrystal samples will be made in this part.

1. Prepare a cuvette containing approximately 3ml of water. This will be called 'reference'.
2. Prepare four cuvettes each containing approximately 3ml of solution from vial (I)-(IV) respectively.
3. Measure the absorption spectrum of each sample following the procedures in the next section.
4. Plot all four spectrum in Excel, print out the data and see the correlation between the amount of KBr added and wavelength of the peak absorption. The larger the nanocrystal, the longer the peak absorption wavelength.

c) *Discussions*

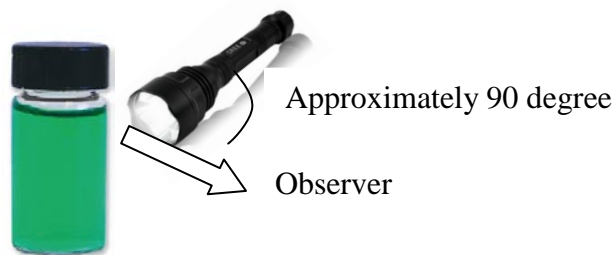
Discussions can be made on the following points.

1. How to interpret UV-Vis absorption spectrum and what information does it contain.
2. Approximate color visually perceived vs. wavelength of light.
3. Larger Ag nanocrystals absorb strongly at longer wavelengths than smaller nanocrystals. Can the relationship between the amount of KBr added and the peak absorption wavelength explained?
4. Measure the absorption spectrum of each sample by following the procedures in the next page.

d) Optional experiment

If time permits and intense white light source is available (e.g., intense LED flash light or halogen light that can produce reasonably directed beam), students can observe the plasmon scattering.

The scattered light can be best observed in darker room in the illumination and observation angle shown below.

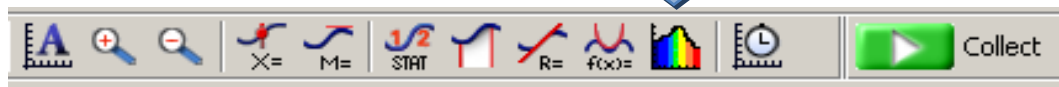


Note: Below is an example photo of the Ag nanocrystals synthesized following the procedures describe here. Individual results (colors) may vary slightly.

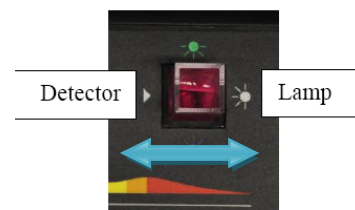


Using the Spectrometer and Software (LoggerPro)

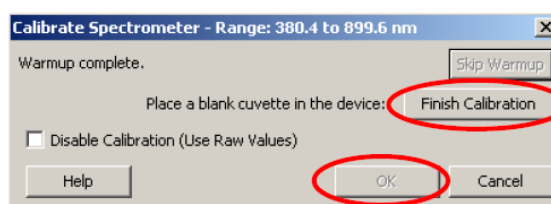
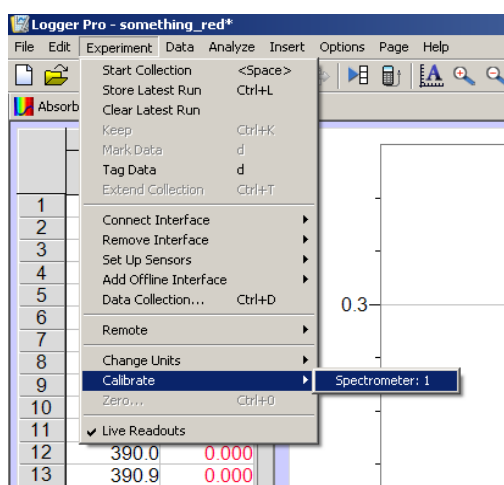
1. Connect the spectrometer to the remaining USB port of PC and start LoggerPro.
2. Mode setup (measurement vs. wavelength)



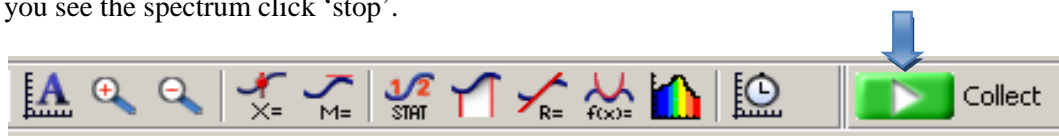
3. Place the cuvette containing water in the cuvette holder. This will be called 'Reference' (see the next page for more information). Cuvette should be filled to about 2/3 of the height. The cuvette has two clear sides and two frosted sides. Clear sides should face the direction the arrow is indicating.



4. Calibrate by clicking the 'Calibrate' under 'Experiment'. It will take about 1 minute to finish calibration. Once the calibration is over, click on 'Finish calibration'. Once the calibration is finished, remove the reference cuvette.



5. Place the 'sample' cuvette in the cuvette holder and start collecting the data by clicking the 'Collect' button. Once you see the spectrum click 'stop'.



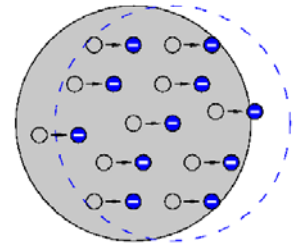
6. Save the data. You can also export the data to csv format that can be read and plotted in MS Excel.
7. Repeat the step 5 and 6 for all the samples.

Origin of the absorption from silver nanocrystals – Plasmon

Plasmon is collective oscillation of conduction band electrons in metals.

In metallic nanoparticles, it can be visualized as in the figure

in the left, it is called localized surface plasmon. The frequency of oscillation of the localized surface plasmon of silver nanocrystals is in the range of visible color in the electromagnetic spectrum and varies with the size of the nanocrystals. When white light (e.g., light from tungsten lamp or the sun) impinges on the metal nanocrystals, the spectral component of the light that corresponds to the frequency of the plasmon is strongly scattered. The spectrum of plasmon can be measured either in the absorption measurement as in this experiment or scattering measurement.



The figure on the left shows the Lycurgus cup from Roman times, which contain metal nanocrystals in it. Its color looks different depending on whether the light source illuminating the same cup is outside (left cup) or inside (right cup). The left cup looks green, which shows the color of the scattered light from the nanocrystals when the cup is illuminated from outside of the cup. The right cup, which has the light source inside the cup, looks reddish, since the green component of the white light is absorbed by the nanocrystals and the rest (red component) is transmitted.

http://www.nature.com/nphoton/journal/v1/n4/fig_tab/nphoton.2007.38_F1.html

Principles of absorption spectroscopy

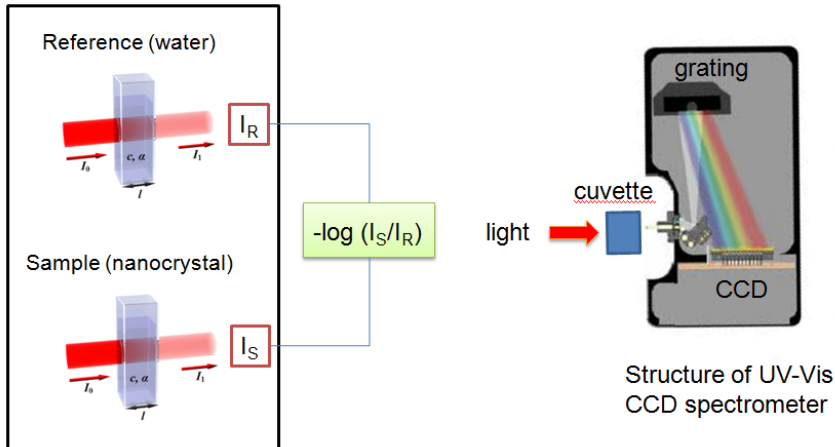
Absorbance (A) is defined as the negative of the logarithmic ratio of the transmitted light intensities between the reference (I_R) and sample (I_S), $A = -\log(I_S/I_R)$. The value of A is a measure of how strongly the material is absorbing the light at a given wavelength. The absorbance (A) follows the Beer's law.

$$A = \epsilon bc$$

ϵ : Molar absorption coefficient

b : optical pathlength of the sample (1 cm for the cuvette)

c : molar concentration of the sample



Spectrometer is a device that measures the absorbance as a function of wavelength. It is composed of light source, sample cuvette holder and detector. Many modern compact spectrometers use CCD (charge coupled device - the same device many digital camera uses as its sensor) as the detector. Usually grating is used to disperse the light and the intensity of the light at different wavelength is detected at different location on the CCD chip.