Analytical Cumulative Exam – Spectroscopy of and with Ag & Au Nanostructures

Prof. L. Hanley, Jan. 2005

1. (15%) Portable Raman spectrometers are now sold by several companies for rapid chemical identification of various chemicals. Describe an experiment and type of nanostructure that could be used to enhance the utility of these instruments for the analysis of species that are soluble in a liquid solvent. Do NOT describe a Raman spectrometer (that is not the question).
2. Describe an experiment to determine each of the following properties of a series of gold nanostructures (i.e., spherical quantum dots) suspended in a solvent, assuming their size ranges between 1 and 100 nm? This experiment must have been demonstrated experimentally somewhere, although you do not need to cite those prior experiments here.
    a. (10%) size distribution
    b. (10%) crystallographic ordering (if any)
    c. (10%) valence band structure (i.e., spacing between high occupied and lowest unoccupied molecular orbitals)
3. Answer the following questions based upon the Mie theory expression for the extinction coefficient of a spherical metallic nanoparticle for the extinction coeafficient E(λ) in the long-wavelength limit:

$$E(\lambda) = [24\pi N_A a^3 \varepsilon_m^{3/2}] \cdot [\lambda \ln(10)]^{-1} \cdot [\varepsilon_i] \cdot [\, (\varepsilon_r + 2\varepsilon_m)^2 + \varepsilon_i^2]^{-1}$$

    where N_A is the areal density of the nanoparticles; a is the radius of the nanoparticle; λ is the wavelength; ε_m is the dielectric constant of the surrounding medium; and ε_i and ε_r are the imaginary and real parts of the metal dielectric function.

    a. (10%) Why does the electronic structure of quantum dots of a given size change when they are placed in different chemical environments?
    b. (10%) Under what conditions of the above equation does one perform surface plasmon resonance with nanoparticles? Explain your answer.
    c. (10%) What advantages does one gain in surface plasmon resonance using Au nanoparticles compared with Au films?
    d. (10%) How does the above equation to describe shifts in UV/Vis absorption that occurs when you stick two nanoparticles together, i.e. by DNA linkers? Assume for simplicity that the nanoparticles that are stuck together also form a sphere.
4. (15%) A recent paper has described how gold nanoparticles have been substituted for traditional organic acid matrix compounds for matrix assisted laser desorption ionization mass spectrometry. What is one required property of the nanoparticles and what is the advantage of their use here?