CUMULATIVE EXAMINATION IN ANALYTICAL CHEMISTRY

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This examination will focus on the analytical characterization of nanometer-sized alkanethiol monolayer-protected gold clusters (MPCs). These are unusual materials that have required the application of an unusually diverse array of analytical methods. (Note: allow yourself no more than 15 minutes per question; items requiring a response have been emboldened).

1. (10 points) The clusters are prepared by the method of Brust in which HAuCl₄ is reduced with NaBH₄ in the presence of alkanethiol. The gold clusters have an average core diameter of about 1.6 nm and their surfaces are decorated with about 50 thiol chains. Unlike bare gold clusters, the monolayer-protected clusters can be repeatedly isolated by evaporation of solvent followed by redissolution, i.e., they are "processable".

The first analytical technique that was applied had as its purpose the determination of the size of the MPCs. That technique was scanning electron microscopy (SEM). Describe the principles of SEM including a rough sketch of the instrument. Identify the various components describing each in as much detail as you know. Why is the instrument called a "scanning" microscope? In the interpretation of the data, the investigators have reported that SEM gives the diameter of the gold core, not that of the entire MPC. Why? From the results you have seen in the literature on SEM of MPCs, estimate the fineness of resolution of the modern SEM instruments that were used.

2. (10 points) Various techniques have been applied to characterize the alkanethiol "coating" of the gold clusters. For example, evidence for there being about 50 thiols attached to each cluster was obtained by thermogravimetric analysis (TGA). Describe this technique in as much detail as you can. Explain in detail how the data obtained could be used to deduce the number of thiols attached to each cluster.

3. (10 points) Infrared absorption was also used to characterize the alkanethiols. The samples were either "drop thin films" on KBr plates or MPCs "pressed in a KBr pellet". Explain these sampling techniques. The infrared data were used to infer structural information about the alkyl chains. Specifically, it was concluded that the long-chain thiols showed mainly an "all-trans" configuration but the short-chain thiol layers contained more "gauche defects". These have to do with the relative intensities and positions of the symmetric (d') and antisymmetric (d') methylene stretching frequencies. Sketch the "all trans" configuration and show a "gauche defect". Explain as much as you know about how the methylene frequencies are interpreted to obtain the desired structural information.

4. (10 points) Mass spectrometry has been used in various ways to characterize the clusters. For example, a thermal desorption source was used to study dodecanethiol-protected gold clusters and it was found that over a narrow range of probe temperatures (240-246 °C), a prominent signal occurred at m/z = 402. Describe the nature of a thermal desorption source. What causes ionization in the source? Identify the ion that is most likely responsible for this peak (atomic weights: C = 12 Da; H = 1 Da; S = 32 Da, Au = 197 Da). Interpret the result that the m/z = 402 ion appears only after the temperature reaches 240 °C.
5. (10 points) A second application of mass spectrometry employed a "laser desorption-ionization" source with a time-of-flight mass analyzer. The laser source was a frequency-doubled Nd:YAG laser ($\lambda = 532$ nm, pulse width = 5 ns). Describe as completely as you can the processes occurring in this laser desorption-ionization source. Also describe in some detail the timing of ionization, acceleration, and detection in the time-of-flight instrument. This method is suitable for high molecular weight species, $m/z = 28$ kDa and $22$ kDa being detected in one example. The former is thought to contain about 145 gold atoms and the latter about 110 gold atoms. What does this tell you about the fate of the sheath of alkanethiol groups during ionization (atomic weights: C = 12 Da; H = 1 Da; S = 32 Da; Au = 197 Da)?

6. (10 points) NMR has also been used to characterize MPCs. In one example, $^1$H NMR spectra showed methyl proton (terminal methyl group) resonances whose full-width at half-maximum ($v_{\text{FWHM}}$) (a) increases with increasing alkyl chain length and (b) increases with increasing solvent viscosity. Explain these two observations in terms of the nuclear relaxation phenomena that are relevant to $^1$H NMR.

7. (10 points) When studied by electrochemistry, the dispersion of MPCs show behavior characteristic of "quantized double-layer capacitances". The model for this concept is a concentric-sphere capacitor with the inner sphere being the gold core and the outer sphere being the interface between the terminal methyls of the alkanethiol chains and the solution. The dielectric (alkanethiol layer) is assumed to have an effective dielectric constant, $\varepsilon$, of 3.0. The following expression was derived for the capacitance of each cluster, $C_{\text{CLU}}$:

$$C_{\text{CLU}} = 4\pi\varepsilon_0\varepsilon(r/d)(r + d)$$

where $\varepsilon_0$ is the permittivity of free space, $r$ is the radius of the core and $d$ is the thickness of the alkanethiol layer.

Taking the fundamental equation for capacitance of a parallel plate capacitor in terms of the area of the plates (A) and the distance between them (m), derive the above equation for the cluster capacitance:

$$C = \varepsilon_0\varepsilon A/m$$

Hint: If you try an integration, remember that the capacitance, $C_s$, of a series combination of individual capacitors, $C_i$, is

$$1/C_s = \Sigma(1/C_i)$$

8. (10 points) The two principal electrochemical experiments that have been performed are slow-scan cyclic voltammetry and differential pulse voltammetry.

(a) Sketch the type of current-voltage curve that is seen in cyclic voltammetry of the MPCs. Be certain to identify the position of zero current along the ordinate. The potential where the current on the positive-going sweep is displaced from zero an amount equal and opposite to the current on the negative-going sweep can be used to identify an important characteristic of the clusters. What is it?

(b) Sketch the type of current-voltage curve that is seen for differential pulse voltammetry. If done correctly, your plot will show a series of peaks, each one similar to
the reversible voltammetric response that one would obtain for a small molecule such as ferrocene. Explain as completely as you can what the authors think is happening to the clusters that diffuse to the electrode as the potential is made negative with respect to the characteristic potential mentioned in 8a. What happens when the potential is scanned in the positive direction?

9. (10 points) The scanning tunneling microscope (STM) has been used to measure "coulomb staircases" of individual cluster particles. Explain as completely as you can the construction and operation of an STM. Explain what is done when the "coulomb staircase" is measured and sketch the form of the plot being certain to label the axes.

10. (points) In your reading you have undoubtedly found a large number of papers describing MPCs (and other metal clusters) and their properties. Apart from the inherent scientific interest engendered by these unusual materials, what do you think the practical applications of them will be, if any?