Self assembly and layer-by-layer deposition

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1 Objectives

- To obtain a working understanding of the self-assembly of (Au) nanoparticles on a solid (silica-glass slide) support

- To demonstrate the self-limiting characteristics of the monolayer self-assembly

- To determine the spectroscopic parameters of the particles in the monolayer, their extinction coefficients and the wavelength dependence of their maximum absorption on the solvent.

- To demonstrate layer-by-layer deposition of the Au/SiO_2 interchanging layers.

2 Introduction

The strategies to obtain self-assembled monolayers (SAM's) of molecular entities as well as the chemical principles that lead to their formation and structures have been described in the previous experiments and their corresponding narratives. Here we will adopt similar principles to self-assemble monolayers of nanoparticles (NP's) and from there proceed to deposit layer-by-layer monolayers of the particles. Thus, the particles in our assembly provide the functionality of "superatoms" and in many senses behave like atoms that otherwise would constitute a conventional lattice. We will demonstrate that no more than one monolayer of NP's is deposited when the synthetic conditions are judiciously selected to limit the deposition to a single layer. We will explore the properties of the monolayer (mostly spectroscopic because of time limitations), compare them to the ensemble of particles dispersed in solution but will show that condition may be chosen so that the particles maintain their single particles identity (size and spectra). We then will proceed to build several monolayers one on top of the other again, monolayer at a time and without destroying the particles identities. However, we emphasize that the degree of interaction between the particles either laterally within the layer or perpendicularly between the layers is to a large degree within our control. We are often able to decrease the distance

between the particles so that electronic (and electric) as well as spectroscopic interactions between neighboring particles affects their properties.

Significant effort is currently invested in attempts to assemble nanostructured materials onto substrates, to study their novel properties, and to investigate some of their potential device and process applications. Among nanostructured materials Au NP's are attractive candidates for building SAM's because of their well-controlled preparation methods, relatively narrow size distribution, good dispersion in various solvents, and unique optical and electronic properties. Several strategies were developed to assemble Au particles on substrates, for example, organic functional groups can be used to link Au particles to the substrate. In another approach, a polyelectrolyte can be employed to immobilize Au particles onto surfaces via electrostatic interactions between the polyelectrolyte and the surface on one side and the polyelectrolyte and the particle on the other side. These methods have advantages over vapor deposition techniques or Langmuir-Blodgett monolayer approaches in the low cost of instrumentation and high throughput of layer fabrication. For potential applications, the formation of dense SAM's is desirable and variable methods attempted to accomplish high density of particles in the layers. However, coverage of immobilized Au particles on substrates is often limited by the repulsive forces between the particles and not by their actual cross-section. These repulsive forces can be attributed to the charge of stabilizers around the particles; the same charge that may keep the particles from agglomeration in the solution. In the present Experiment we will use a mixed-bed ion exchange resin to remove most of the stabilizer from the Au sol leading to a relatively dense Au film on a glass slide substrate (albeit relatively unstable suspension).

Layer-by-Layer (LBL) will be utilized to construct 3D multilayer films. The interparticle distance and the thickness between layers are critical in controlling the optical properties of such "artificial solids". Interparticle distance can be varied by changing particle size and coverage, therefore, control of the thickness between layers is intensely investigated in contemporary nanoscience research. One approach that will be utilized here is to control the distance between the Au NP's thin-film layers is to control the thickness of the intervening silica layer between the Au layers. Another strategy is to coat each Au particle with a silica shell whose thickness can be varied. Yet another method is to vary the number of polymer bilayers between Au particle monolayers. In methods that utilize silica to separate the Au-NP layers, condensation-polymerization of silicate is the method of choice to grow silica layers or shells. Here we employ this method to build a SiO_2 layer in between the Au-NP's monolayers.

The dielectric environment surrounding the particles critically affects the optical properties of Au thin films or NP's. Mie was first to describe the correlation between the wavelength position of the plasmon band of a metallic particle and the dielectric constant of the medium in 1908. For metallic particles, when the radius (we restrict our Experiment to spherical particles only) of the metallic particle, R, is much smaller than the wavelength of the incident light so that $\frac{R}{\lambda} \leq 0.01$, quasi-static approximation can be assumed. With such approximation, phase shifts, i.e. retardation effects of the electromagnetic field over the

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particle diameter are negligible. This means that the generally multipolar excitations of Mie theory are restricted to the dipolar electric mode. Thus, Mie theory is simplified considerably and leads to Equation 1:

$$\sigma_{ext}(\omega) = \frac{12\pi\omega}{c}\epsilon_m^{\frac{3}{2}}R^3\frac{\epsilon_2(\omega)}{[\epsilon_1(\omega) + 2\epsilon_m]^2 + \epsilon_2(\omega)^2} \tag{1}$$

where σ_{ext} is the extinction cross section, ω is the angular frequency of the incident light, c is the speed of light, ϵ_m is the dielectric function of the embedding medium, V_o is the particle volume and ϵ_1 and ϵ_2 are the real and imaginary parts o fthe dielectric function of the particle material, respectively. Resonance happens at the frequency where the denominator $[\epsilon_1(\omega) + 2\epsilon_m]^2 + \epsilon_2(\omega)^2$ is at a minimum. That is, when $\epsilon_1(\omega) = -2\epsilon_m$. Thus, the plasmon absorption is proportional to $\epsilon_m^{\frac{3}{2}}$ according to Mie theory.

The position of the plasmon absorption peak depends on the dielectric constant of the surrounding medium according to the following equation
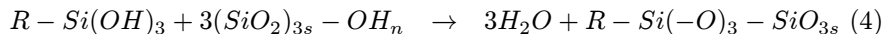
$$\lambda^2 = \lambda_p^2(\epsilon^\infty + 2\epsilon_m) \tag{2}$$

where λ_p is the metal's bulk plasma wavelength, ϵ^∞ is the high-frequency dielectric constant due to interband and core transitions, and ϵ_m is the surrounding medium dielectric constant. Thus, the square of the position of the plasmon band changes linearly with the dielectric constant of the medium. This dependence provides the rationale for a sensing technique that detects the presence of biological moieties at the surface of the metallic particles (called Surface Plasmon Resonance, SPR). When these non-polar moieties adsorb on a layer of metallic particles from an aqueous solution, the position of the plasmon shifts. We will test this dependence in the present Experiment.

3 Self assembled monolayer of gold nanoparticles

The surfaces of Au particles have little affinity to glass surfaces, the former are highly hydrophobic while the latter are very hydrophilic. The surfaces of silica and most other oxides in water are covered by hydroxide or hydronium ions but those of metallic particles are covered by ions that originate from the precursor to the metallic particles or externally added stabilizers (e.g., citrate in our case). Therefore, in general, a primer molecule is used to link Au particles to SiO_2 surfaces. The chemicals used for primers have two functional groups. One side is a silane group and the other side is usually a mercapto or an amine group. We will use aminosilane bridges, from 3-aminopropyltrimethoxysilane, (APS), $NH_2(CH_2)_3Si(OCH_3)_3)$, or the very similar primer, 3-aminopropyltriethoxysilane (APTES, $NH_2(CH_2)_3Si(OC_2H_5)_3)$. The first step in both cases is hydrolysis of the alcohol side to give a silanol head

group followed by condensation polymerization of the latter with the -OH groups at the surface of the glass to anchor the primer onto the glass, Reactions 3 and 4. Note that the subscripts s mean solid or surface.

$$(EtO)_3Si - R + 4HOH \quad \rightarrow \quad 4EtOH + R - Si(OH)_3 \qquad (3)$$

$$R - Si(OH)_3 + 3(SiO_2)_{3s} - OH_n \quad \rightarrow \quad 3H_2O + R - Si(-O)_3 - SiO_{3s} \ (4)$$

The relative rates of the hydrolysis vs. the rate of condensation are determined by the polarity of the solvent used (mixtures of water-alcohol) and the pH of the solution. This motif of hydrolysis-condensation of silane precursors repeats itself in many of the processes that require siloxane binding to oxides, as we shall see later.

To condition the glass, the slide is immersed in 1% APS and then in a 0.5 mM Au sol to anchor Au particles on the glass. No adsorption of Au onto glass occurs if the Au particles are coated first with an APS monolayer and then the glass is immersed in the Au-APS sol. This is because chemical adsorption of the amine on the Au surface is much faster than the silane condensation reaction. Because the particles collisions with the walls are infrequent condensation of $-SiOH$ groups from the bridging molecules among themselves dominate then.

Figure 1 shows the spectrum of the product monolayer on the glass slide, as well as an AFM image of that monolayer at the end of the deposition. In spite of the seemingly dense coverage, only 25% of the available surface is covered with Au NP's. The heavy coverage seen in the Figure is a distortion of the AFM images in the X-Y plane caused by tip tilt. Nonetheless, this coverage is higher than the highest coverage reported in the literature. The inset of Figure 4.1 shows that the plasmon absorbance of Au film on the glass levels off in 20 min. This is the self-limiting monolayer coverage. Note that none of the sample shows any absorption of light in the red and NIR spectral range. This is an indication that the electronic interparticle interactions are weak. When the distance/diameter ratio between the particles is smaller than 1 strong absorption bands (scattering to be exact) can be observed at longer wavelengths similar to the extinction spectra of nanorods. You may have noticed that during the Turkevic sunthesis of Au particles the solution turn blue-violet before it becomes red-wine. The blue color is caused by absorption/scattering of light in the red. This may indicate that the particles at the beginning of the synthesis are larger than later on. **Any suggestions to explain how could it happen?**

4 Procedures:

4.1 Particle preparation:

Prepare a solution of Au NP's using the Turkevic method as described earlier. This generates Au particles of 15 nm in size. To repeat: 400 mL of water containing about 0.1 g $HAuCl_4 3H_2O$ are heated to boiling, and 50 mL 1% sodium
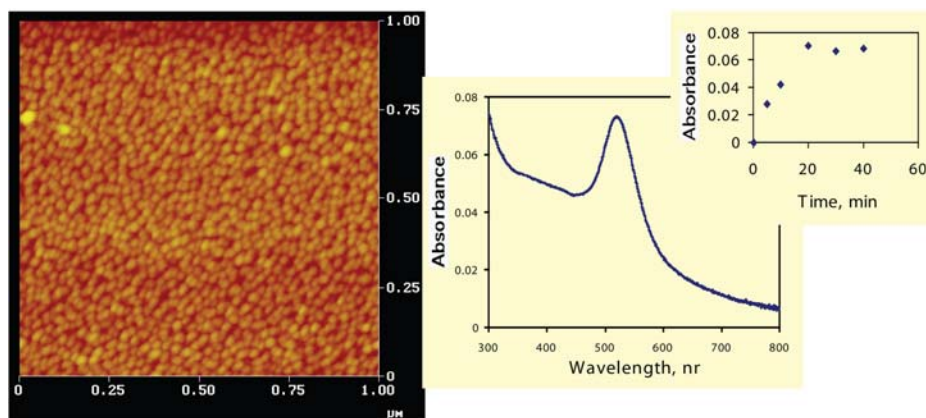
Figure 1: UV-Vis absorption spectrum of a monolayer of 15 nm Au NP's (right) and an AFM image of that monolayer. The plasmon band is centered at 520 nm. The top insert shows the time-evolution of absorbance at 520 nm in min. The absorbance reaches a constant level at 20 min.

citrate is added to the boiling solution under vigorous stirring. The solution is boiled for additional 20 min, and the volume is adjusted to 500 mL after cooling. The obtained sol is wine red and Au concentration is approximately 0.5 mM (in atoms per L). Assuming their size is indeed 15 nm, what is the concentration of the particles?

To get better adsorption of Au on glass, much of the citrate anions at the particles' surface must be removed. This is achieved by adding 8 g of ion exchange resin (Amberlite MB-150, Sigma-Aldrich) to the 500 mL Au sol under stirring. The initial conductivity of the sol is about 1000 S/cm and the final conductivity should be controlled in the range of 6-20 S/cm. The Au sol with much of the citrate removed is not stable for long periods of time and the color changed to blue after several days. Therefore, measure the absorption spectrum ASAP or do not remove the stabilizer before you are ready to proceed. The adsorption of Au particles from the resin treated sol in the following steps is fast and a relatively dense monolayer is then obtained.

4.2   Conditioning of the glass and anchoring the particles:

Glass slides (pre-cleaned quartz micro slides, from Gold Seal Products, or Premium Cover Glass, from Fisher) is cleaned with 95% ethanol containing KOH and then washed with water. To activate the glass surface, the glass is immersed into 0.54% silicate solution overnight. The glass is then immersed into 1% APS in water for 3-4 hr and then washed with water. The APS solution is somewhat turbid and it must be freshly made to prevent it from becoming transparent, which means that condensation occurred in the solution. To immobilize Au

particles, the APS functionalized glass is immersed into resin treated Au sol to obtain an Au monolayer. Measure the evolving monolayer by measuring the spectra until saturation is achieved.

4.3   Effect of medium on spectra:

To study the effect of different solvents on the plasmon absorption of Au particles, the glass slide with the Au monolayer is immersed in the desired solvent for half an hour and then it is transferred into a cuvette which contains the same solvent and the spectrum is measured. Between each measurement, the glass should be rinsed and immersed into a solvent that is miscible with both the previous solvent and the next one. For example, after the bromobenzene measurement the glass is rinsed and immersed in ethanol and then it is rinsed and immersed in hexane for the next measurement. Thus with this strategy one can use one glass to get the effect of many solvents on absorption from a single preparation with little mechanical or chemical changes in the particles. Table 1 lists several common solvents. Choose four of these solvents (in addition to water and air). Find their dielectric constant in the Handbook of Physics and Chemistry. Measure the absorption spectra of your monolayer-covered glass slide immersed in each of these four solvent. Report your results in a graph.

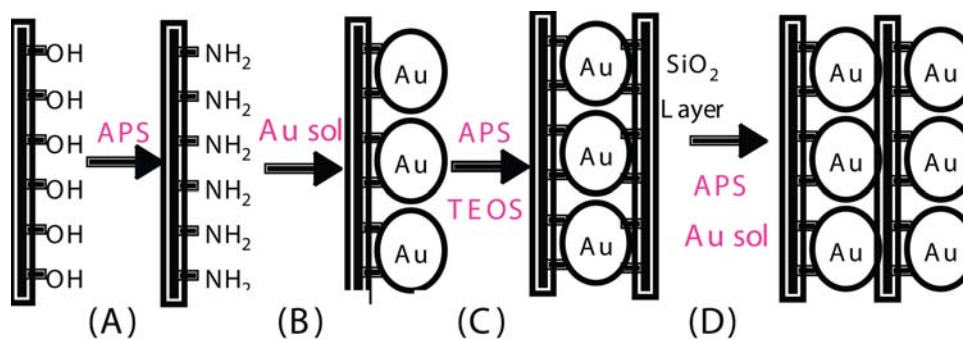# 5   Layer-bylayer deposition; $Au - SiO_2 - Au$

Figure 2: Schematic strategy to obtain Layer by Layer deposition of Au/SiO2. A) Conditioning the glass slide with the APS primer. B) Attaching Au particles to the amine head groups of APS. A monolayer of Au particles is created. C) Treating the Au monolayer with APS. The amine of APS attaches to the particles. TEOS is added to generate a layer of silica. D) The silica is treated with APS to repeat step A and the process continues to deposit any number of monolayers.

Polycondensation of silicate is used as a sol-gel process applied to the prepa-

ration of glass ceramics and in the synthesis of silica particles. The procedure was developed by Stober in 1968 and is often called after its discoverer. The condensation reaction rate can be controlled by changing the alkyl chain length of the alcohol component in the solvent mixture and by changing silanes. Methanol and tetramethyl-orthosilicate (TMOS) are found to react the fastest. Here we employ this process to form silica layers in between the Au NP's layers. The strategy is illustrated in Figure 2. The silicate and alcohol to be used are tetraethyl-orthosilicate, (TEOS), $Si(OCH2CH3)_4$ and ethanol, respectively and ammonia is used to provide basic pH, which catalyzes the reaction. The complete hydrolysis of TEOS and the complete condensation of the hydrolysate can be represented by equations analogous to Eq. 3, 4. The repeating steps are clearly outlined in the caption to Figure 2.
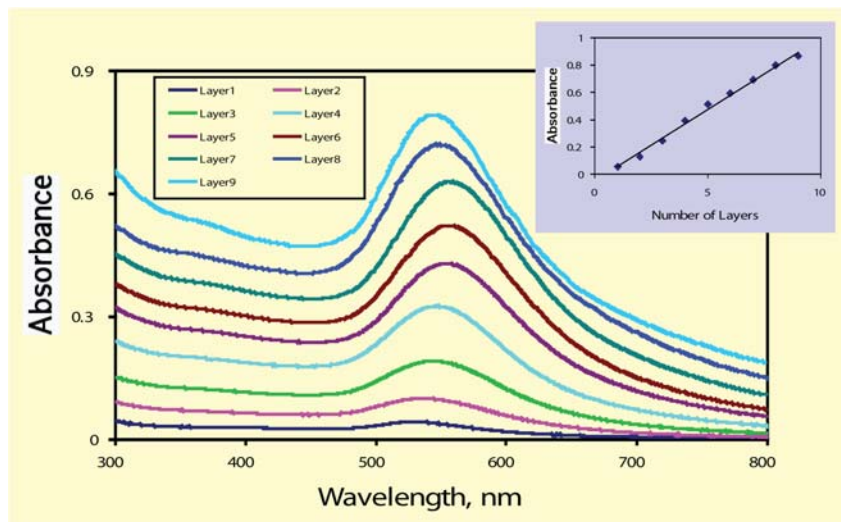

Figure 3: Absorption spectra of consecutively deposited 9 layers of Au/SiO2 on glass. The insert illustrates the linearity of the contribution of each layer to the absorbance at the peak of the plasmon band, indicating the reproducibility of the self limiting monolayer deposition in each step. However, some shift in the position of the bands can be observed from layer to layer, probably due to particle-particle interactions across neighboring layers.

Figure 3 shows absorption spectra of 9 layers of Au particles on glass prepared by the above strategy and the inset shows the plot of absorbance at the plasmon band peak against the number of Au layers. The plot is averaged from 6 samples and it shows the linear increase in absorbance for all samples as the number of Au layers increases. This linearity indicates that the particle coverage is homogeneous and constant.

Other combinations of molecular bridges can also be utilized. Dithiol molecules can link the second layer of Au particles on top of the first one and thus

form repetitive multilayers of Au films. The thickness between layers is then controlled by the length of the alkyl chain, but, in general, measurement of such thickness is beyond common experimental accuracy. Similarly, different concentrations of diamine molecules (e.g., 1,3-diaminopropane, $NH_2(CH_2)_3NH_2$ were used to obtain multilayer-Au films.

The thickness between layers and intralayer roughness can have a significant effect on the dipole-dipole coupling of the plasmon mode interlayer and intralayer between the Au particles. If the distance between layers is short, the dipole interaction shifts the Au plasmon band to the red. But if the insulating layer is thick, no dipole interaction is induced any more and the interaction is shielded.

5.1 Procedures:

Using the monolayer of Au particles prepared above, follow the steps described below and outlined in Figure 2.

5.1.1 Deposition of SiO_2 layer:

The glass slide containing the Au monolayer is first immersed into 1% APS for 3 hr. This is followed by immersion in TEOS solution preferably overnight. The TEOS solution is prepared by adding 0.4-0.5 mL TEOS and 2 mL ammonia into 500 mL 4:1 ethanol:water solution. This procedure forms a silica layer on top of the Au monolayer. The glass is then immersed in 1% APS again for 3 hr and in resin-treated Au sol for 3-4 hr. Thus a second Au layer was anchored onto the silica layer. The above procedures is repeated as time permits. The glass must be rinsed with water thoroughly after each immersion.

5.1.2 Layer-by-layer (LBL) measurements:

After each deposition of Au NP's measure the spectrum and demonstrate the deposition of a single monolayer.

6 Points to consider in your report:

1. Since you know the concentration of Au in the initial solution you can determine how much was adsorbed on the slide and how much constitutes a monolayer. Since the spectra on the glass (in water) is similar to that of the solution you may assume that the size remain the same. What percentage of the surface is covered with gold? What is the extinction coefficient and how does it compare to the solution? Report both in the solid-state physics convention of natural-log (rather than log10) and cross sections in units of per atoms/cm^3. Do your particles interact electronically with one another within a layer?

2. Does the position of the wavelength of the plasmon band follow the Mie theory's predictions?

3. How much absorbance is added by each monolayer of Au NP's.

7   Additional reading:

Layer by Layer Deposition:

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- Decher, G., "Fuzzy Nanoassemblies: Toward Layered Polymeric Multi-composites." Science 1997, 277, (29), 1232-7. Grabar, K. C.; Freeman, R. G.; Hommer, M. B.; Natan, M. J., "Preparation and Characterization of Au Colloid Monolayers." Anal. Chem. 1995, 67, 735-43.

Spectroscopy of NP's, primarily metallic:

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- Ung, T.; Liz-Marzan, L. M.; Mulvaney, P., "Optical properties of thin films of Au@SiO2 particles." J. Phys. Chem. B 2001, 105, (17), 3441-3452.

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- Stober, W.; Fink, A.; Bohn, E., Controlled growth of Monodisperse Silica Spheres in the Micron Size Range. J. Coll. Interface Sci. 1968, 26, 62-9.

Table 1: Absorbance and plasmon peak position of an Au monolayer in different solvents

	Solvent	Dielectric constant	Wavelength (nm)	Absorbance
1	Air			
2	Water			
3	Acetone			
4	Ethanol			
5	Hexane			
6	Ethylene glycol			
7	1,3-propanediol			
8	Toluene			
9	Nitrobenzene			
10	Bromobenzene			